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Supercritical Fluid Regeneration of Adsorbents

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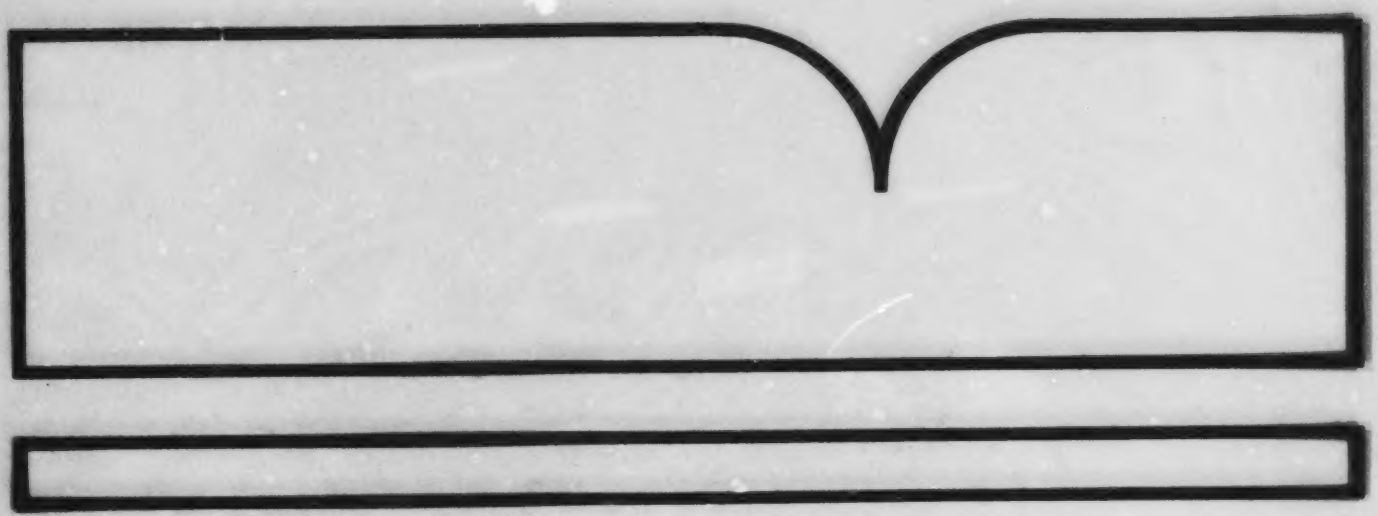

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May 1983

SUPERCRITICAL FLUID REGENERATION OF ADSORBENTS

by

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Cooperative Agreement No. CR-806874-01

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16. ABSTRACT The report gives reults of a program: (1) to perform studies supercritical (fluid) carbon dioxide (SCF CO2) regeneration of adsorbents, using samples of industrial wastewaters from manufacturing pesticides and synthetic solutions; and (2) to estimate the economics of the specific wastewater treatment regenerations, based on test data. Processing costs for regenerating granular activated carbon (GAC) for treating industrial wastewaters depend on stream properties and regeneration throughput. Costs, including capital amortization, were estimated for two cases: $0.14-0.29/lb GAC for atrazine and dinitro butylphenol wastewaters with GAC throughputs of 2000-5000 lb/day. Thermal regeneration costs are about $0.29-0.36/lb GAC for low-capacity plants, based on rotary kilns as the lowest-capital alternative. Using laboratory solutions of phenol, alachlor, and acetic acid, synthetic resin adsorbents showed good working capacities and rapid and complete desorption of solute when the adsorbent was properly selected to treat a solute according to molecular weight, water solubility, and polarity. A preliminary economic comparison indicated that, in certain cases, resin adsorbents would have substantially lower compression requirements, compared to GAC, for the removal and recovery of an organic component from a liquid stream.

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ABSTRACT

The principal objectives of this program were:

- to perform studies of supercritical carbon dioxide (SCF CO_2) regeneration of adsorbents, which had been used to adsorb organics from industrial wastewaters from manufacturing pesticides and synthetic solutions.
- to estimate the economics of the specific regenerations, based on test data.

Processing costs for regenerating granular activated carbon used to treat industrial wastewaters depend on wastewater properties and regeneration throughput. SCF CO_2 regeneration costs, including capital amortization, were estimated for two cases: \$0.14/lb of carbon for atrazine (5000 lb GAC/day), and \$0.29/lb of carbon for dinitro butyl phenol (2000 lb GAC/day). Thermal regeneration costs have been estimated at about \$0.29-0.36 (3) per pound of carbon for low-capacity plants, based on rotary kilns as the lowest-capital alternative.

Using laboratory solutions of phenol, alachlor and acetic acid, synthetic resin adsorbents showed good working capacities and rapid and complete desorption of solute when the adsorbent has been properly selected to treat a solute according to molecular weight, water solubility, and polarity. A preliminary economic comparison indicated that in certain cases, resin adsorbents would have substantially lower compression requirements, and thus lower energy costs, when compared to activated carbon for the removal and recovery of an organic component from a liquid stream.

ACKNOWLEDGEMENT

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I. INTRODUCTION

A. Objectives

In June, 1979, Arthur D. Little, Inc. entered into a cooperative agreement with the Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. The objectives of the program were to perform studies of supercritical carbon dioxide (SCF CO_2) regeneration of adsorbents used to treat samples of industrial wastewaters from manufacturing pesticides and synthetic solutions, and to estimate the economics of the specific regenerations, based on test data.

In recent years, granular activated carbon has been used increasingly to remove organics from industrial wastewaters. In many cases, carbon and other adsorbents have been used to remove specific toxic chemicals prior to biological treatment. Often high molecular-weight toxic materials are selectively adsorbed relative to low molecular-weight biodegradable compounds. Thus, adsorbents may have more extended run lengths, because the adsorption system may be designed to remove predominantly the lower concentrations of toxics, rather than the complete spectrum of organics present.

A major inhibition to the broader use of adsorbents has been the cost and operating difficulty of regeneration methods for restoring capacity after saturation. For carbon, by far the most commonly used agent, thermal regeneration processes are common. However, energy requirements, on the order of 10,000 Btu/lb of carbon, are high. In many cases, carbon must be replaced at a rate of 5-20% per regeneration due to losses, further increasing cost. Depending on regeneration throughput, capital costs may be high, and the operation of some thermal systems, such as multiple-hearth furnaces, is difficult to control. This sometimes leads to loss of an entire furnace charge (1).

When synthetic resin adsorbents are used, solvent regeneration methods must be employed because of lack of tolerance of high temperatures by the adsorbent. Liquid solvents, such as acetone and methanol, must be recovered for recycle, resulting in the need for distillation to remove the desorbed chemicals and residual water from the solvents. As a result of high costs, liquid solvent regeneration cannot be used in many cases, thereby ruling out synthetic resins as adsorbents.

Because of these constraints, supercritical carbon dioxide (dense-phase at elevated pressures) was proposed and tested as a solvent for regeneration. CO_2 is a reasonably good organic solvent; its effectiveness for stripping adsorbates is varied: low molecular-weight organics are removable to different degrees, depending on chemical nature and regeneration temperature and pressure. It has been found that adsorbent working capacity must be measured experimentally after multiple adsorption-regeneration cycles, and the economics must be compared on a case-by-case basis (2).

Thus, this program was directed toward evaluating adsorbent-regeneration for a number of pesticide manufacturing wastewaters and synthetic solutions to provide the basis for estimates of process economics.

B. Approach

A wide range of pesticide manufacturing companies was contacted by telephone to determine whether potential candidate wastewaters for carbon treatment and SCF CO_2 regeneration were available. Sources were drawn from government publications and discussions with personnel at the EPA Industrial Environmental Research Laboratory, Research Triangle Park, NC.

In addition to pesticide manufacturers, contacts were made with chemicals manufacturers. Also, organizations offering carbon regeneration processes or equipment for sale were contacted, including the Calgon Division of Merck, Pittsburgh; Envirotrol, Inc., Pittsburgh; Zimpro, Inc., Rothschild, Wisconsin; and Illinois Water Treatment Company, Rockford, Illinois. Prior to this program phase, the major activated carbon manufacturers or developers were contacted, including Westvaco, Kennecott, Amoco, and Calgon.

The results of these discussions were specific expressions of interest from several pesticide and chemicals manufacturing companies.

1. A manufacturer of agricultural chemicals had provided samples of wastewater from the production of atrazine for a preliminary study reported previously (2). For this program, based on presentation of results of the preliminary work, a second sample of wastewater was shipped for further laboratory evaluation, plus engineering and economic estimates of process requirements. That study is reported in Section VB.

2. Vicksburg Chemical Company, a division of Vertac, Inc. provided samples of wastewater from the production of dinitrobutylphenol (DNBP). The laboratory and economic evaluation of these samples is presented in Section VA.

3. A Midwestern chemical company provided a combined wastewater from their South Carolina plant for preliminary experimental testing. Principal products from this plant included aromatic resins, although the wastewater composition was not specified. The results of the tests are given in Section VC.

In parallel with studies on specific wastewaters, a program was undertaken to test the adsorption-regeneration characteristics of certain synthetic resins, using laboratory-synthesized solutions of chemicals that had been characterized in the prior research and development program (2). This work was carried out in cooepration with Illinois Water Treatment Company, and the results are summarized in Section VI.

II. CONCLUSIONS

A. Wastewater Studies

1. Processing costs for regenerating granular activated carbon for treating industrial wastewaters depend on the specific stream properties and the regeneration throughput. Costs, including capital amortization, were estimated for two cases, based on laboratory data on carbon working capacity:

Wastewater	Regeneration Throughput lbs GAC/day	Processing Cost, $/lb GAC (mid-1980)
Dinitro butyl phenol	2000	0.29
Atrazine	5000	0.14

2. Thermal regeneration costs have been estimated about $0.29-0.36 per pound of carbon for low-capacity plants, based on rotary kilns as the lowest-capital alternative (3). However, comparison with thermal regeneration cannot be made without corresponding data on the working capacity of thermally-regenerated carbon. Because the adsorption capacity of regenerated carbons from the SCF process may differ from that of thermal regeneration, the daily use rate of carbon, for a given waste-stream flow, and thus the daily cost, may differ.

3. The attainable steady-state working capacity of carbon with SCF CO_2, typically lower than virgin capacity, can only be determined by testing with wastewater samples, as done in this project.

B. Laboratory Synthetic Resin Adsorption-Regeneration Studies

1. Using laboratory solutions of phenol, alachlor and acetic acid, synthetic resin adsorbents showed good working capacities and rapid and complete desorption of a solute when the adsorbent has been properly selected to treat a solute according to molecular weight, water solubility, and polarity.

2. A preliminary economic comparison indicated that resin adsorbents would have substantially lower compression requirements compared to activated carbon for the removal and recovery of an organic component from a liquid stream. This would result in energy cost savings of 71-83% over activated carbon.

III. RECOMMENDATIONS

1. The SCF CO_2 process should be tested at pilot or small commercial scale, on the order of 1000 lbs/day of adsorbent throughput.

2. For synthetic polymeric and carbonaceous resins:
   a. Bench-scale studies should be expanded to include a broader range of adsorbents and adsorbates.
   b. Further model studies should be performed to help verify the present understanding of the physical and chemical processes that occur in adsorption and desorption.
   c. Long-term effects of multiple cycling on the adsorbents should also be investigated to provide sufficient data for a complete economic evaluation.

IV. BACKGROUND

A. Rationale for Supercritical-Fluid Regeneration

For many applications, thermal regeneration of activated carbon is the only method presently available to recycle spent carbon for reuse. There is a significant loss of carbon during the thermal treatment due to oxidation of the carbon and attrition of fines. The make-up carbon necessary to compensate for the losses is a significant factor in the overall cost of activated carbon treatment. In addition, energy consumption is high, on the order of 10,000 Btu per pound of carbon (3).

Desorption of solutes with conventional liquid solvents has received considerable attention. The consensus is that the rate of desorption is slow and the extent of solute removal is solvent-dependent. In addition to problems associated with slow desorption and low solute removal, liquid solvent regeneration has other drawbacks. Commercial solvents are relatively expensive and must be recovered for reuse. Consequently, solutes must be removed from the solvent after desorption. For moderately volatile solutes, recycle of solvent will require extensive distillation. Furthermore, many conventional solvents are health hazards in themselves. If the solvent is air- or steam-stripped from the carbon, the stripping agent may require further processing to avoid emission of air pollutants.

For efficient and economic regeneration of activated carbon, the desired solvent characteristics are (i) high solubility for the adsorbates, (ii) favorable mass transfer properties for rapid desorption and (iii) high volatility for subsequent separation of solutes. Liquid solvents exhibit high solubility but slow diffusion. In the gas phase, mass transfer is rapid, but solubilities are very low. Fluids in the region of their critical temperatures and pressures, called supercritical fluids (SCF), represent a good compromise. It has been found that activated carbon and other adsorbents can be regenerated efficiently by desorbing adsorbates with supercritical fluids (2).

B. Supercritical Fluids

The supercritical fluid region can best be visualized with the aid of Figure IV-1, a vapor pressure curve. All pure substances have vapor pressure curves, the points that form the curve being those conditions where liquid and vapor phases may co-exist, i.e., boiling points. For all substances, there is a temperature and pressure on this curve above which separate liquid and vapor phases no longer exist. This is the critical point, and the region beyond this point is called the supercritical fluid region.

The most common supercritical fluid used in activated carbon regeneration is carbon dioxide. The critical point of carbon dioxide is 31°C (87.8°F) and 72.9 atm (1072 psia), well within conditions in use in the chemical process industries. Above this temperature and pressure, carbon dioxide is in the supercritical state and exhibits the properties of a supercritical fluid. An example of the solubility power of supercritical fluids is shown in Figure IV-2, which gives the solubility of naphthalene in carbon dioxide. Below the critical pressure (gaseous carbon dioxide), very little naphthalene dissolves. However, as the pressure is increased into the supercritical region, the solubility of naphthalene rises sharply above 6 g/liter at 100 atm.

C. Regeneration Process Description

A schematic diagram of the process using a supercritical fluid to regenerate activated carbon is shown in Figure IV-3a. The four basic components are a regeneration vessel, a pressure reduction valve, a separator, and a compressor for recycling fluid. Ancillary pumps, valving, fluid make-up, and other equipment such as heat exchangers for heating or cooling are omitted from the figure for clarity; in a batch-continuous system for regeneration, for example, multiple vessels might be used, one in a regeneration mode while another is being filled or unloaded.

Figure IV-3b is a plot giving extensive data on the solubility of naphthalene in carbon dioxide as a function of temperature and pressure; Figures IV-3a and IV-3b illustrate closed-loop operation of the regeneration

FIGURE IV-1

VAPOR PRESSURE CURVE

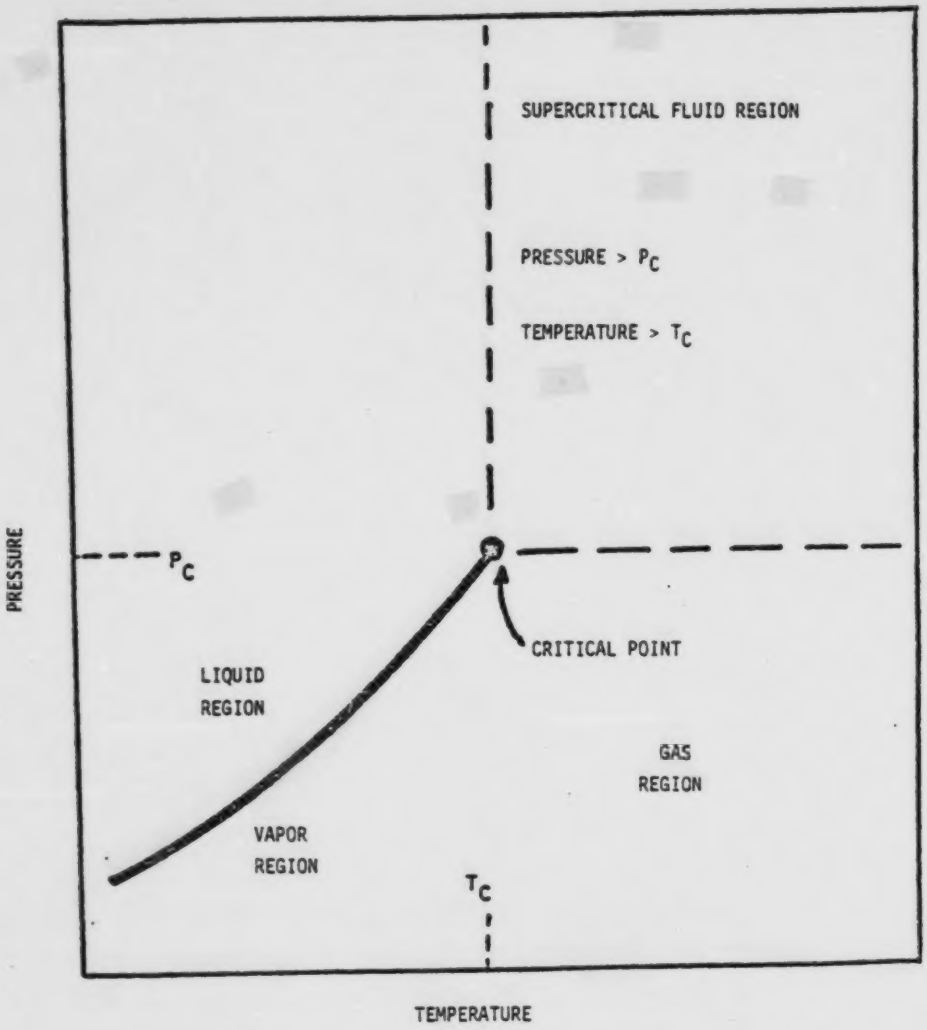


FIGURE IV-2

SOLUBILITY OF NAPHTHALENE IN SUPERCRITICAL FLUIDS

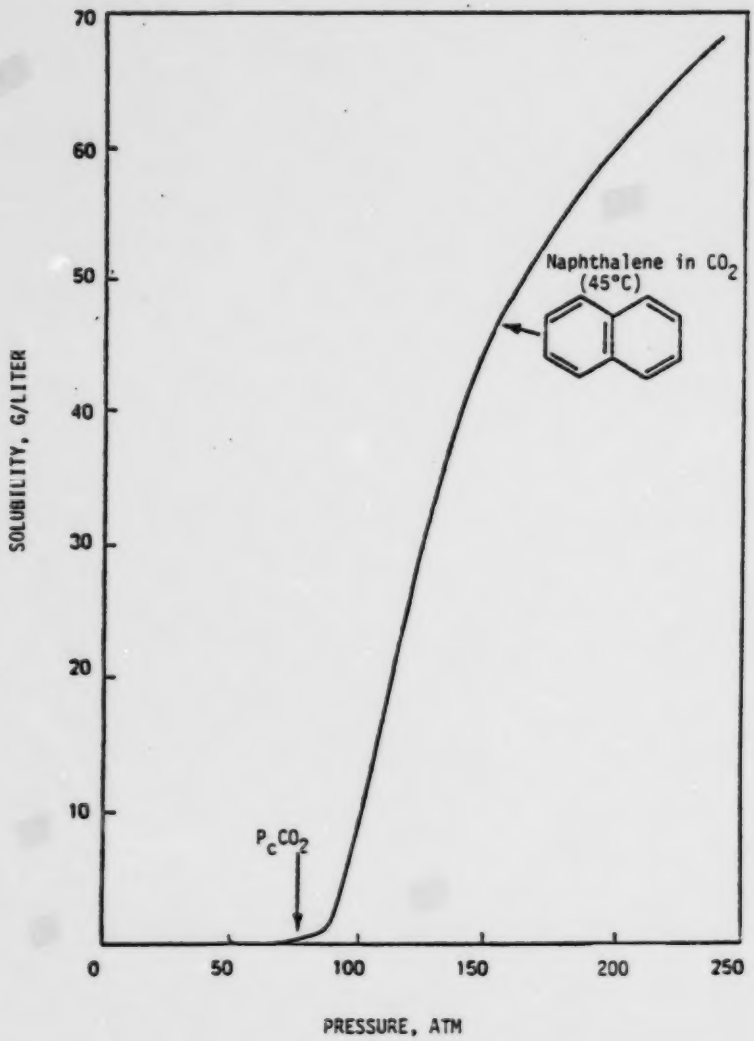


FIGURE IV-3a

SUPERCRITICAL FLUID
EXTRACTION PROCESS
(ADSORBENT REGENERATION)

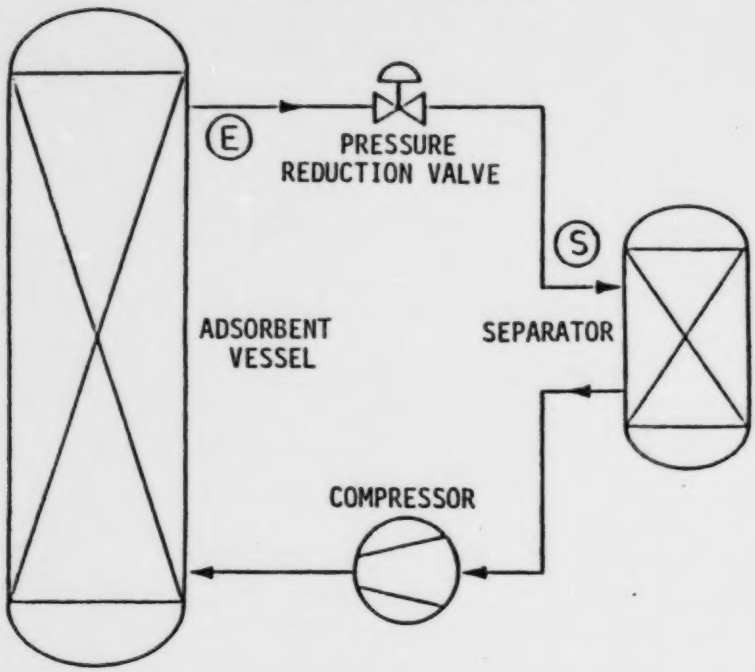
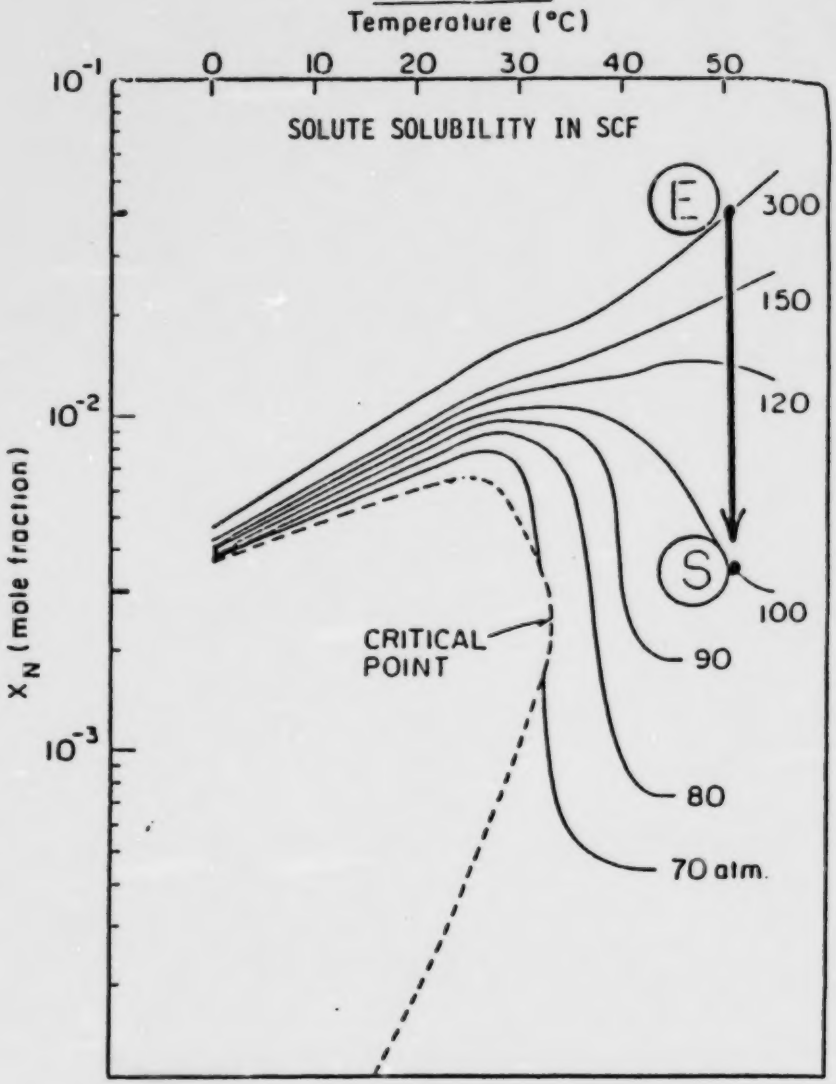


FIGURE IV-3b


Temperature (°C)
0
10
20
30
40
50
10^{-1}
10^{-2}
10^{-3}
SOLUTE SOLUBILITY IN SCF
X_N (mole fraction)
E
S
300
150
120
100
90
80
70 atm.
CRITICAL POINT

process. Two points are indicated on two solubility isobars in Figure IV-3b, (E) representing regenerator conditions and (S) separator conditions. In the example, supercritical carbon dioxide at 300 atm and 50°C is fed to the regeneration vessel where it dissolves (desorbs) the material from the carbon. The carbon dioxide-naphthalene stream is expanded to 100 atm through the pressure reduction valve (as indicated by an isothermal path in Figure IV-3b), the precipitated naphthalene formed during the expansion is collected in the separator, and the carbon dioxide is recompressed and returned to the regenerator. The process continues until all the adsorbate is removed.

D. Prior Research and Development

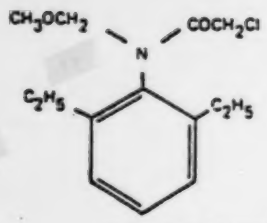
Various industrial wastewater applications that have been studied (2) include six pesticides: alachlor, atrazine, carbaryl, pentachlorophenol, trifluralin, and diazinon. The molecular structure of these compounds is given in Figure IV-4.

To determine the effectiveness of SCF regeneration for cleaning carbon loaded with these pesticides, wastewater solutions were passed through bench-scale carbon columns and the concentration of pesticide leaving the column was measured, as shown graphically in Figure IV-5.

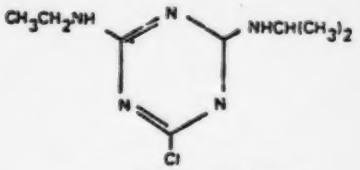
In the initial stages of adsorption, nearly all of the pesticide is adsorbed by the carbon. As the carbon becomes loaded, pesticide begins to break through; this continues until the carbon has adsorbed its limit, and the exit concentration of pesticide is identical to the feed concentration. A direct measure of the amount of pesticide adsorbed by the carbon is obtained by integration of the area indicated by the shaded zone in Figure IV-5. Regenerating that carbon, repeating the adsorption experiment, and comparing the areas of these adsorption breakthrough curves gives a determination of the effectiveness of the regeneration process.

FIGURE IV-4

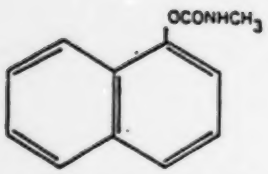
PESTICIDES (AND CLASS) TESTED FOR SOLUBILITY IN CARBON DIOXIDE



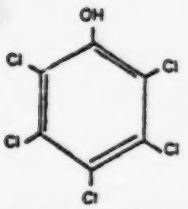
ALACHLOR (Acetanilide)



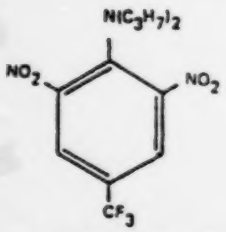
ATRAZINE (Triazine)



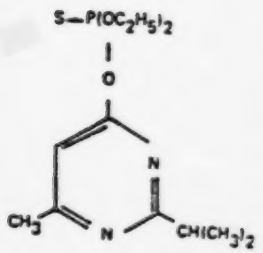
CARBARYL (Carbamate)



PENTACHLOROPHENOL (Chlorophenol)



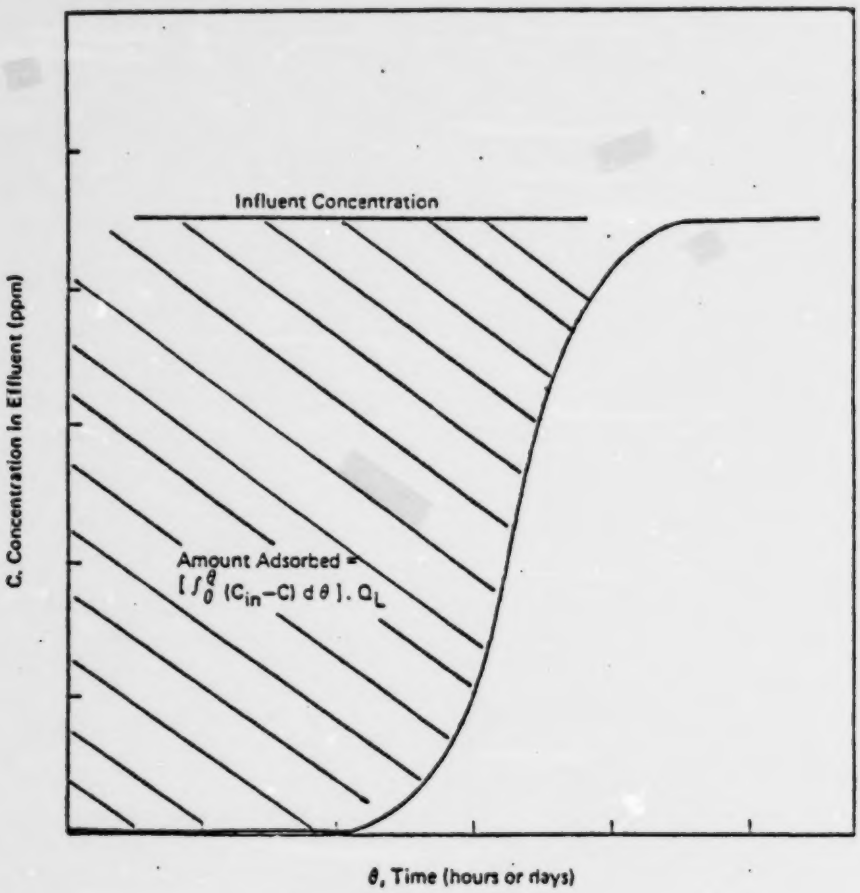
TRIFLURALIN (Nitroaromatic)



DIAZINON (Organophosphate)

FIGURE IV-5

ADSORPTION BREAKTHROUGH CURVE: LOW FLOW RATE


Influent Concentration
Amount Adsorbed =
$[\int_0^{\theta} (C_{in} - C)\, d\theta]\,.\,Q_L$
C, Concentration in Effluent (ppm)
θ, Time (hours or days)

ADSORPTION BREAKTHROUGH CURVE, LOW FLOW RATE Q_L

A series of adsorption breakthrough curves for a synthetic atrazine solution is shown in Figure IV-6. The solid curve to the right shows the adsorption breakthrough on virgin carbon. The various symbols to the left indicate the breakthrough curves of the second to seventh cycle, with an SCF regeneration between each adsorption.

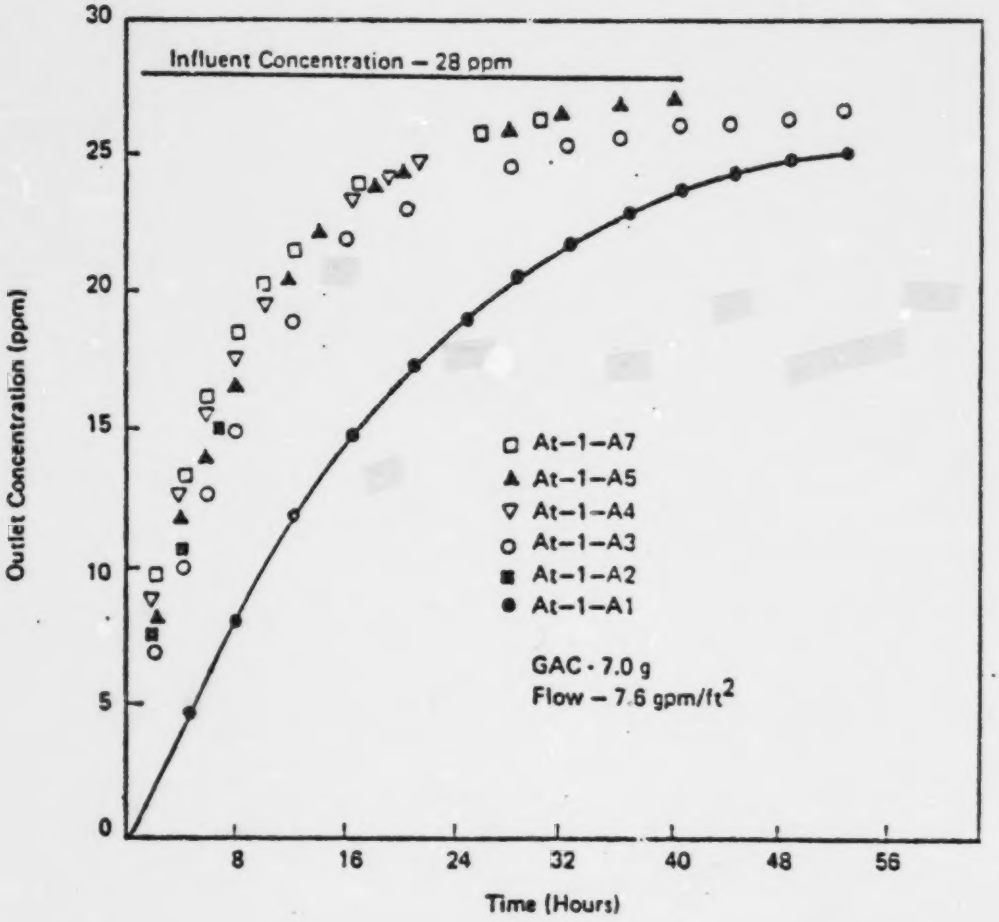
Figure IV-6 indicates approximately one-third of capacity lost in adsorption performance after the first adsorption/regeneration cycle. However, there is little further loss from the second to the seventh cycles. This loss is probably due to "irreversible adsorption": that is, during the first adsorption, some pesticide is strongly adsorbed onto the carbon surface. This fraction of the total material adsorbed is not removed from the carbon during the SCF regeneration process. Nevertheless, although over seven cycles there was a 33% loss in capacity, multi-cycle performance is often better than that of thermal regeneration systems, where there is a 5-10% loss in capacity each cycle (11).

Many independent measurements have shown there is no mass loss of carbon in regenerating with supercritical CO_2.

Thus, these studies showed that SCF regeneration of activated carbon offers an alternative to thermal and liquid solvent regeneration techniques. Using carbon dioxide above its critical point, organics can be desorbed from carbon and subsequently separated from the CO_2 by a simple reduction in pressure.

FIGURE IV-6

ADSORPTION FROM ATRAZINE SOLUTION



V. WASTEWATER STUDIES

A. Dinitro Butyl Phenol Wastewater

1. Introduction

The herbicide 2-sec-butyl-4,6,-dinitro phenol (DNBP) is used to control weeds and grasses, principally in fruit and nut orchards. DNBP is fairly stable, with a shelf life of two years, and has an LD_{50} of 58 mg/kg. It is a potential skin, eye, and lung irritant and must be handled with caution.

The characteristics of the wastewater from manufacturing this herbicide are shown in Table V-1. The total organic carbon (TOC) level is about 20,000 ppm (2.0 wt.%), largely unspecified. Included is about 100 ppm of DNBP, and about 5000 ppm of 2-methylbutyric acid. In addition, there is a high concentration of an inorganic salt, Na_2SO_4. The wastewater was provided by the Vicksburg, Mississippi plant of Vertac, Inc.

A series of experiments was run to determine the effectiveness of supercritical carbon dioxide to regenerate granular activated carbon columns loaded with this wastewater. The plan was similar to that used in previous wastewater studies (2): GAC columns were cyclically adsorbed and regenerated at various process conditions to determine the steady-state working capacity of the GAC.

2. Experimental Methods

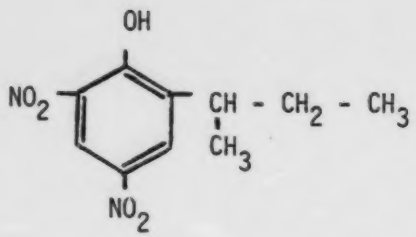
a. Adsorption

A sketch of the adsorption apparatus used is shown in Figure V-1. The GAC used was Calgon F-400, screened to a particle size of -12+30 mesh. The GAC columns used were high-pressure stainless-steel tubes, 0.45 cm ID x 22.9 cm long. Each column was loaded with 7.00 gm of GAC with plugs of glass wool in both ends of the column to prevent spillage. The DNBP wastewater was doubly filtered, first through Whatmann #42 paper filters, then through 0.22 μm Millipore filters. This filtered feed was then pumped

TABLE V-1

DINITROBUTYLPHENOL CHARACTERISTICS

1. Molecular Structure:



2. Wastewater Concentrations (Approximate).

DNBP	100 ppm
TOC	20,000 ppm
Na_2SO_4	20 wt. %
2-methyl-butyric acid	5,000 ppm
pH	6-7

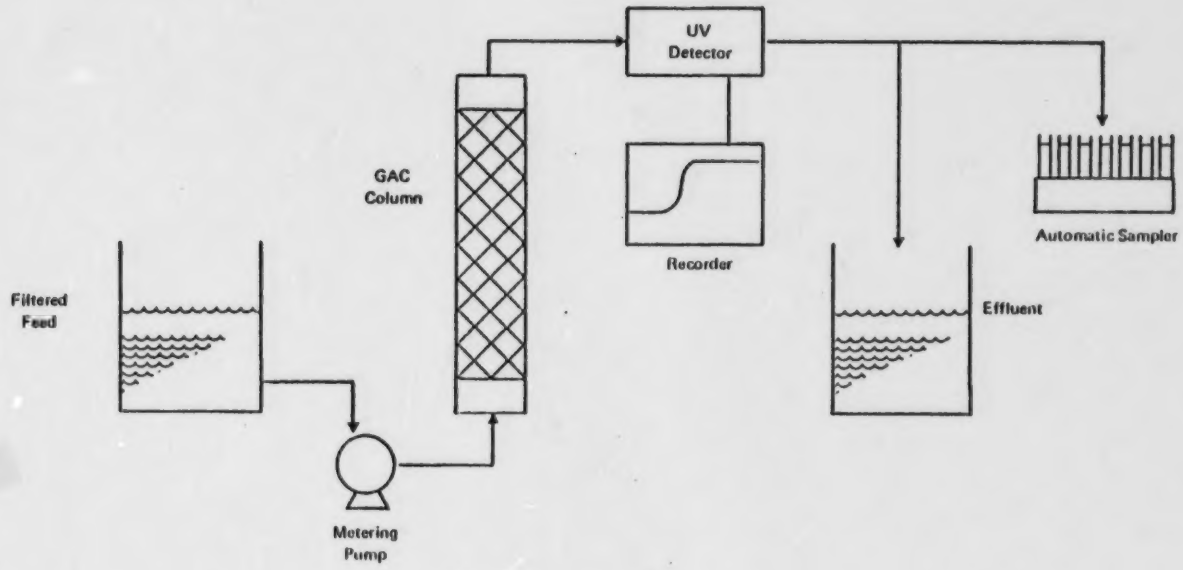


FIGURE V-1

WASTEWATER ADSORPTION APPARATUS

up through the GAC column at a flow of 3.2 ml/min, equivalent to 1.1 GPM/ft^2 of column. In addition, all of the DNBP columns were backwashed with 150 ml of distilled water after the adsorption sequence.

Because of the high concentration and variety of organics in the wastewater, it was found that the concentration of DNBP could not be directly measured by UV spectrophotometry. UV scans of effluent samples of the wastewater showed that at a wavelength of 380nm, the UV absorbance value rose steadily and leveled off in the shape of a characteristic adsorption breakthrough curve. All GAC adsorptions were monitored at this wavelength to determine column performance. This method did not necessarily trace the adsorption of DNBP; rather, it indicated the adsorption of some representative organic species in the wastewater. Breakthrough curves for a three-cycle series are shown in Figure V-2.

In order to check the loadings on GAC, the GAC column was first dried after adsorption and backwashing by flowing low-pressure carbon dioxide through it at 55°C and then weighing the dried column to determine weight picked up during adsorption. This method gave a final number for total weight gained during adsorption. Table V-2 shows weight changes for adsorption and desorption from a three-cycle series.

b. Regeneration

The apparatus for GAC column regeneration is shown in Figure V-3. Carbon dioxide from high-pressure cylinders was compressed at room temperature from a suction pressure of about 70 atm (about 1000 psig) to an operating pressure in the range of 150 to 275 atm (2250 to 4000 psig) by means of a diaphragm compressor (AMINCO Cat. No. 46-13421). The carbon dioxide was then heated above its critical temperature, passed down-flow through the GAC column where the organics were desorbed from the carbon. The CO_2 then was expanded to atmospheric pressure where desorbed material was separated out. Carbon dioxide flow rates were monitored with a Fisher and Porter flowmeter (FP-1/2-27-G-10/83) and total flow during a regeneration was measured with a Singer dry test meter (DTM-200).

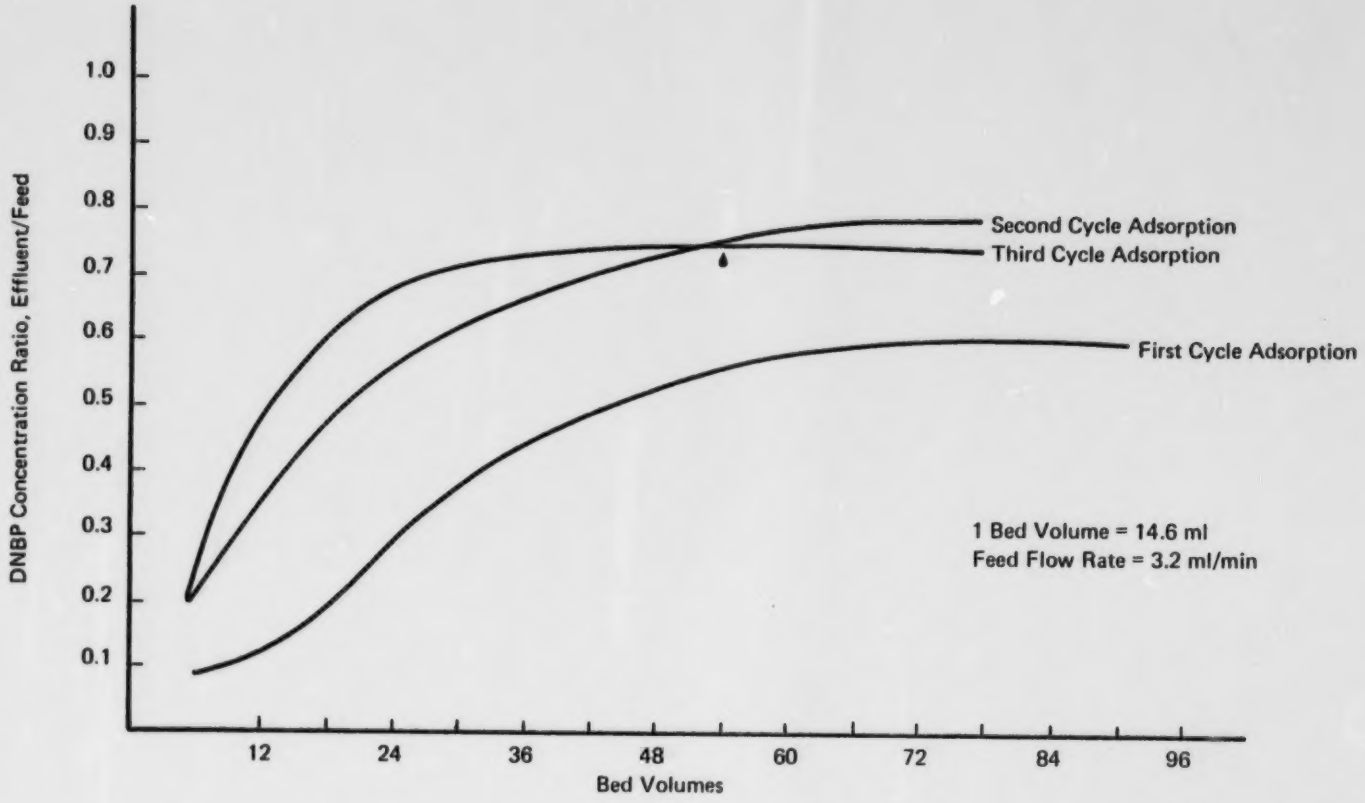


FIGURE V-2 ADSORPTION BREAKTHROUGH CURVES FOR DNBP ON GAC (UV ABSORBANCE AT 380 nm)

TABLE V-2

ADSORPTION AND REGENERATION OF GAC
LOADED WITH DNBP WASTEWATER

Cycle No.	Adsorption[1] Weight Gain, Gms/Gm	Desorption[2] Weight Loss, Gms/Gm
1	0.22	0.11
2	0.18	0.09
3	0.07	-

[1] Net, after backwash and drying.

[2] With CO_2 at 225°C and 275 atm; Cycle 1 with 260 gms CO_2/gm GAC;
Cycle 2 with 520 gms CO_2/gm GAC

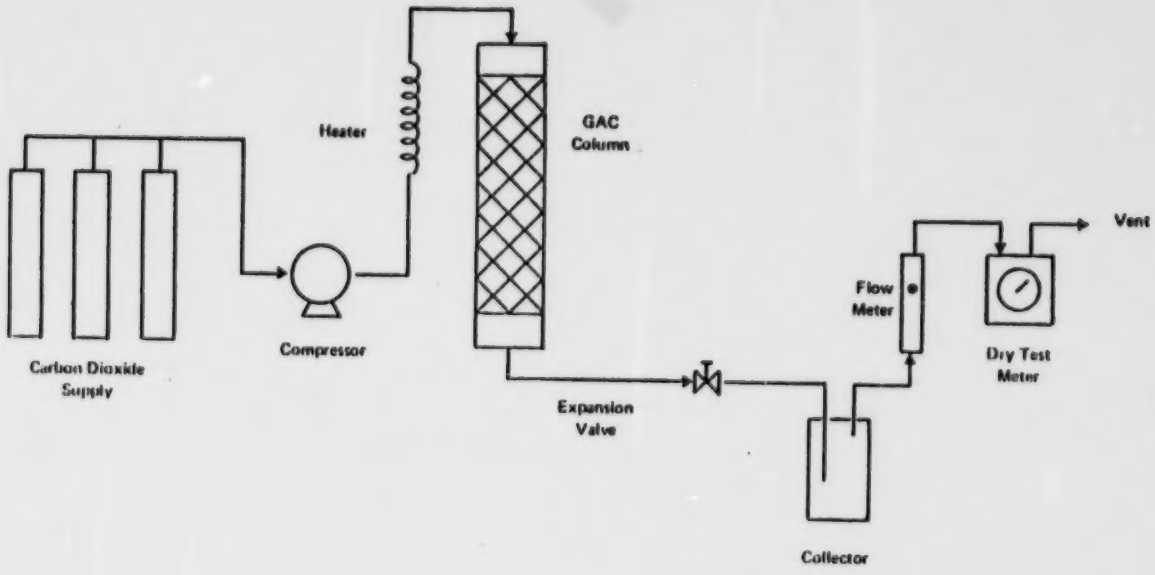


FIGURE V-3

WASTEWATER REGENERATION APPARATUS

The extent of regeneration was determined by direct weighing of the GAC columns before and after desorption. Initially, the weight of material collected in the low pressure separator was also used to determine regeneration, but due to the volatility of some of the organic species present, this was found not to be effective in measuring regeneration performance. Ideally, a CO_2 recycle system such as that studied previously (2) combined with periodic weighing of both carbon column and separated desorbed material would have permitted experimental determinations of solvent amounts required for adequate regeneration, as well as separator conditions. However, such recycle runs are very time-consuming and thus inappropriate for screening studies. Solvent requirements and separator conditions were studied for alachlor and phenol (2), and these were used in the engineering and economic estimates presented in later sections.

3. Experimental Results

Five series of adsorption-regeneration cycles were run. Four of these were performed with the initial sample of DNBP wastewater drawn by the manufacturer in mid-1979. The fifth series was run with a second sample, drawn in late 1979. Based on discussions with the manufacturer, no special preservation means were taken during storage of the samples. Typically, each series consisted of three or four adsorption-regeneration cycles.

Table V-3 summarizes the working capacities achieved; the capacity figures are accurate to about $\pm$ 0.005 lbs/lb. From the results at 225°C, it is evident that increased pressure has a beneficial effect on capacity. The two temperature points at 341 atm show that capacity is higher at higher regeneration temperature.

The series run with the second DNBP wastewater sample was intended as a check of the first low-pressure series with sample #1. The second sample was analyzed by the manufacturer as similar to the first. However, it is evident that a significantly higher working capacity than expected was achieved at 150 atm: 0.042 lbs/lb at 150°C vs. 0.03 lbs/lb at 225°C. Taking into account the positive effect of temperature, the working-

TABLE V-3

ACTIVATED CARBON WORKING CAPACITY

WITH DNBP WASTEWATER

WASTEWATER SAMPLE	REGENERATION CONDITIONS T, °C	P, atm	WORKING CAPACITY, LBS/LB GAC
1	225	150	0.03
1	225	275	0.05
1	225	341	0.06
1	120	341	0.04
2	150	150	0.042

capacity at 225°C should have been greater than at 150°C. Presumably, feed filtration and column backwashing should have eliminated any differences due to suspended solids or dissolved inorganics. It was concluded, therefore, that the two samples were not similar, and it was decided that engineering and economic estimates should be run on the basis of the lower working-capacity figures (sample #1).

One inherent advantage of the SCF regeneration process is the ability to collect material adsorbed on the GAC in a concentrated form. Material collected from the DNBP series was analyzed by infrared spectroscopy (IR), as is shown in Figure V-4. An attempt to identify this desorbed material as pure DNBP was not successful though, as can be seen when the IR trace for DNBP (Figure V-5) is compared with the spectrum of the desorbed material. It cannot be identified as 2-methylbutyric acid, also reported to be present in the wastewater (Table V-1). More likely, the desorbate is a mixture of product, reactants, and derivatives of each, and the spectrum shows features of a number of different chemical species.

4. Engineering and Economic Evaluations

a. Operating Conditions

Prior design calculations in estimating costs of similar regeneration systems have shown that desorber vessel cost for a given volume is a strong function of operating pressure. However, at lower pressures, working capacity of the adsorbent decreases, which increases the vessel volume to process a given loading of wastewater organics per day. Thus, an optimum pressure exists. For the DNBP case, several estimates were run to help decide that pressure level, using the DNBP experimental data for GAC working capacity. The DNBP manufacturer's specification led to a GAC regeneration capacity of 2000 lbs/day. A summary of conditions selected is given in Table V-4.

The GAC working capacity came directly from the data shown in Table V-3.

FIGURE V-4

IR SPECTRUM OF MATERIAL DESORBED FROM GAC LOADED FROM DNBP WASTEWATER

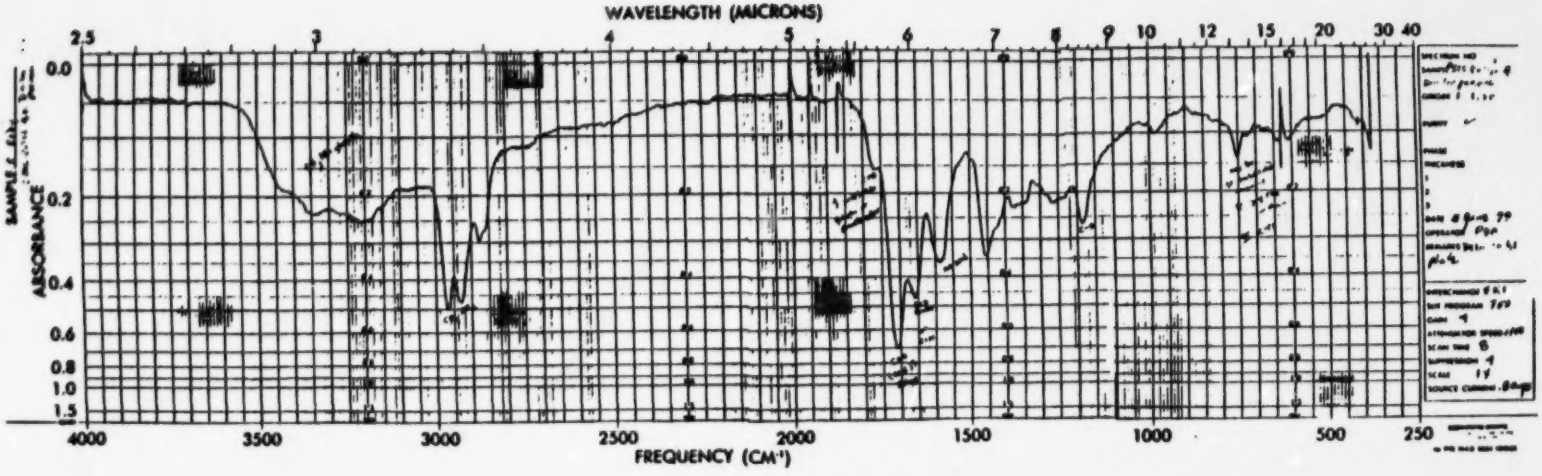
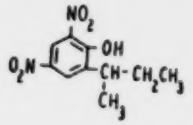


FIGURE V-5

30095K 2-sec-BUTYL-4,6-DINITROPHENOL

$C_{10}H_{12}N_2O_5$ Mol. Wt. 240.22



Source: P. Einhorn,
Rollins-Purle,
Baton Rouge, La.
Capillary Cell: Melt

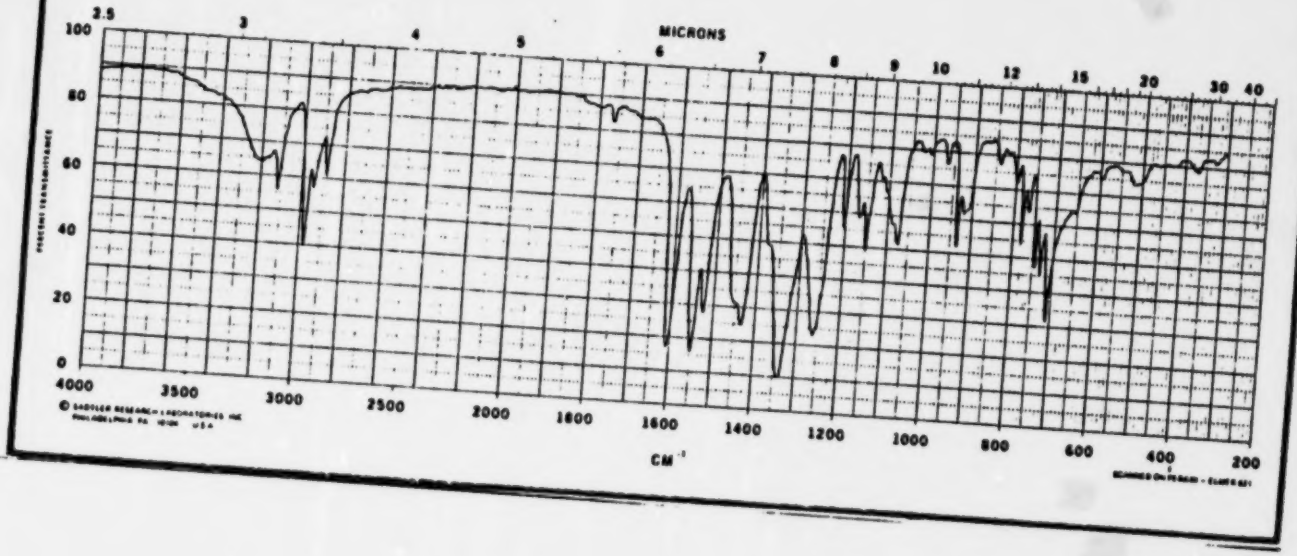


FIGURE V-5 (Cont'd)

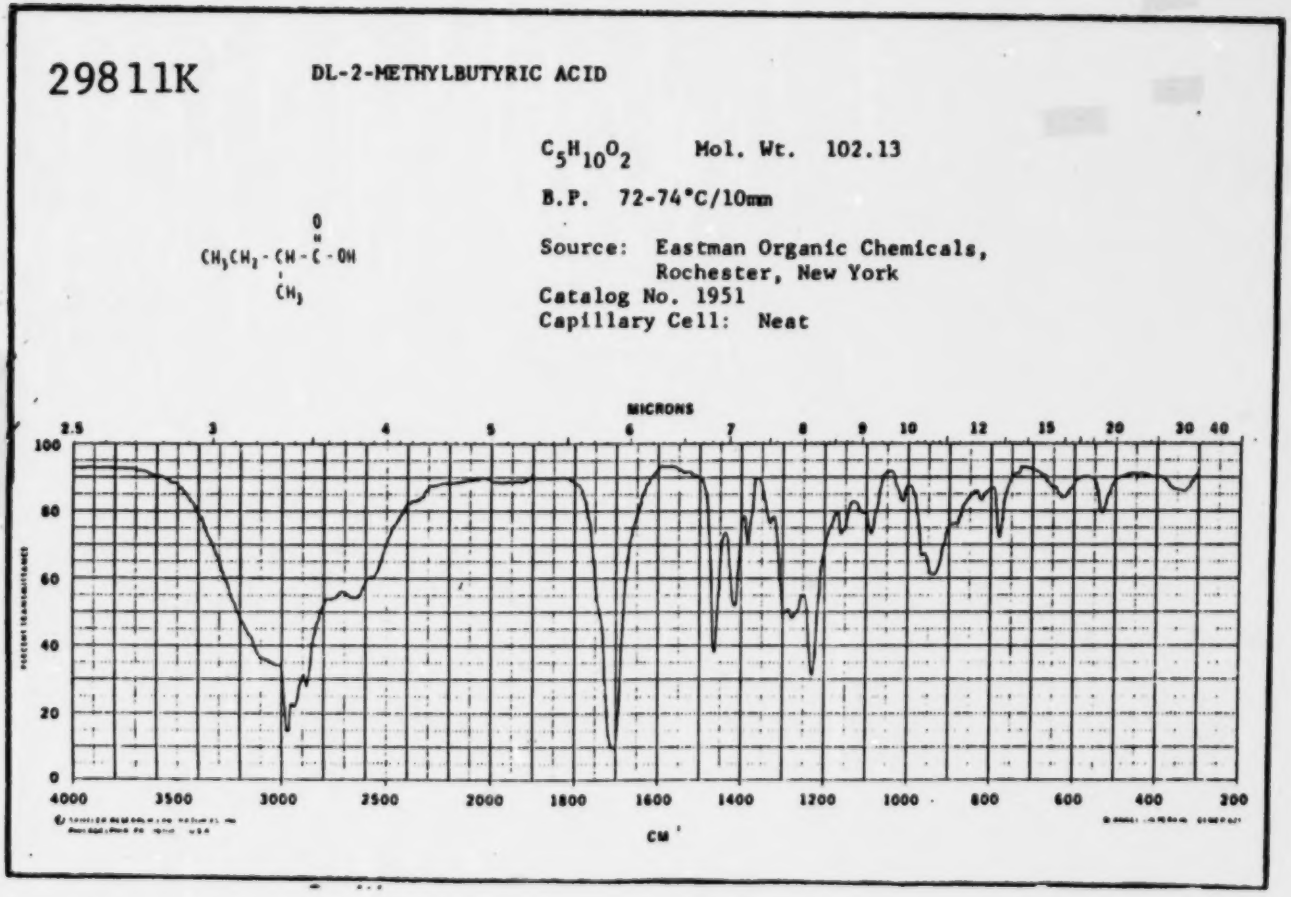

29811K
DL-2-METHYLBUTYRIC ACID
$C_5H_{10}O_2$ Mol. Wt. 102.13
B.P. 72-74°C/10mm
Source: Eastman Organic Chemicals, Rochester, New York
Catalog No. 1951
Capillary Cell: Neat
MICRONS
2.5 3 4 5 6 7 8 9 10 12 15 20 30 40
100 80 60 40 20 0
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200
CM⁻¹

TABLE V-4

DNBP DESIGN CASE

Regeneration Capacity, Lbs GAC/Day	2000
Regeneration Pressure, Atm	275
Regeneration Temperature, °C	225
GAC working Capacity, Lbs/Lb	0.05
Separation Pressure, Atm	120
Separation Temperature, °C	59
CO_2 Flow, Lbs/Hr	2000

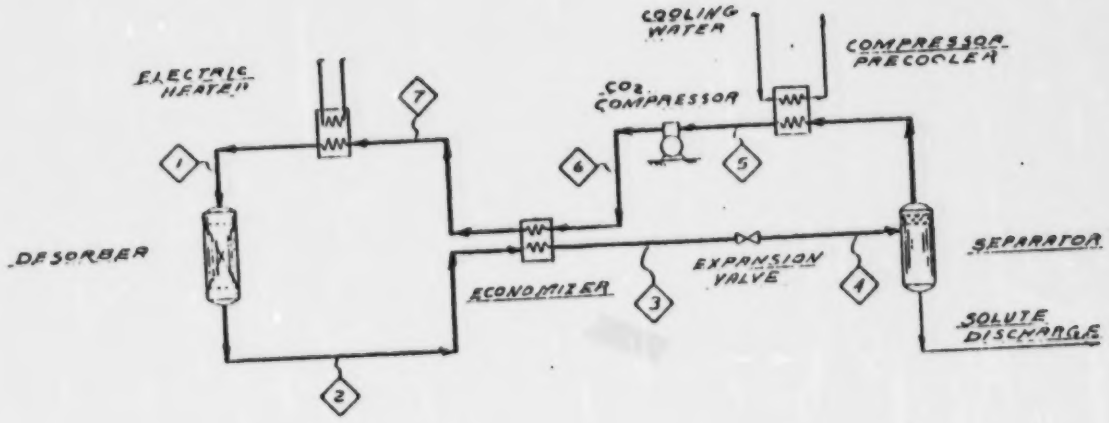
The selection of separator conditions came from the following considerations. Because the extensive experimental work to determine these conditions was beyond the scope of the screening studies, analogous systems were reviewed. First, the manufacturer's objective for the regeneration process with DNBP was to obtain a substantial reduction in DNBP level to permit feeding the effluent to a biological treatment plant; bacterial growth in that plant would otherwise be inhibited or poisoned by the 100 ppm DNBP level in the feed. Thus, the goal was not virtually complete removal of DNBP (e.g., 1 ppm or less), but about a ten-fold reduction to 10 ppm. Because of this, the purity of the recycled CO_2 was less important, and it was assumed that a five- to ten-fold decrease in DNBP-CO_2 solubility would be adequate, comparing desorber and separator conditions.

Second, data are available for the solubility of naphthalene and alachlor in CO_2 (2). In both cases, a pressure decrease from 275 to 120 atm would produce the requisite decrease. Also, at 120 atm in both cases, the solubility does not vary greatly with temperature; therefore, separator temperature was selected primarily to minimize heat exchange costs while providing an adequately low temperature at the recycle CO_2 compressor suction. The optimization calculations led to the choice of 59°C as separator temperature.

The CO_2 flow of 2000 lbs/hr was determined as follows. In prior work with high-pressure (275-atm) regeneration of GAC loaded with alachlor (2), it was found that the desorber effluent concentration (alachlor in CO_2) was reduced more than ten-fold after about 20 pounds of CO_2 were used per pound of GAC. Similar results were obtained for tests at levels of 14-gm and 0.84-lb GAC charges. For the design DNBP system, 2000 lbs GAC are regenerated over a 20-hour day, giving a throughput of 100 lbs/hr. Multiplying this rate by 20 lbs CO_2/lb GAC gives the selected flow rate of 2000 lbs/hr.

Figure V-6 gives a schematic of the overall process, with process conditions tabulated.

FIGURE V-6



STATE POINT	1	2	3	4	5	6	7
LOCATION	DESORBER INLET	ECONOMIZER INLET	EXPASION VALVE INLET	SEPARATOR INLET	COMPRESSOR INLET	COMPRESSOR OUTLET	ELECTRIC HEATER INLET
CO_2 FLOW RATE Lb./HR	2,000	2,000	2,000	2,000	2,000	2,000	2,000
PRESSURE PSIA (BAR)	3990 (275)	3990 (275)	3990 (275)	2174 (120)	2176 (120)	3990 (275)	3990 (275)
TEMPERATURE °F (°C)	437 (225)	437 (225)	166 (74.4)	130 (58.9)	100 (37.8)	131 (55)	387 (197.2)

PROCESS FLOW DIAGRAM
REGENERATION OF ACTIVATED CHARCOAL
BY SUPER CRITICAL CARBON DIOXIDE
(DINITROBUTYL PHENOL CASE)

b. Plant Design and Economics

i) Overall Plant

Figure V-7 gives the process piping and instrumentation diagram.

CO_2 flows through the desorber at regenerating conditions, through an economizer heat exchanger and then through a pressure let-down valve. Based on discussions with suppliers and on internal engineering evaluations, a compressor/expander is uneconomical at the low flows that would be used in small regeneration systems of about 5,000 lbs/day GAC or less.

The expanded CO_2 stream is sent to a separator vessel for solute separation. The separator includes a mesh disengagement section to trap entrained water and adsorbate. Solute (adsorbate) is discharged from the separator as a solution or slurry in the water that has also been stripped from the GAC pores. CO_2, which is still a condensed phase near critical conditions, is pre-cooled, compressed to desorption pressure, and recycled to the desorber.

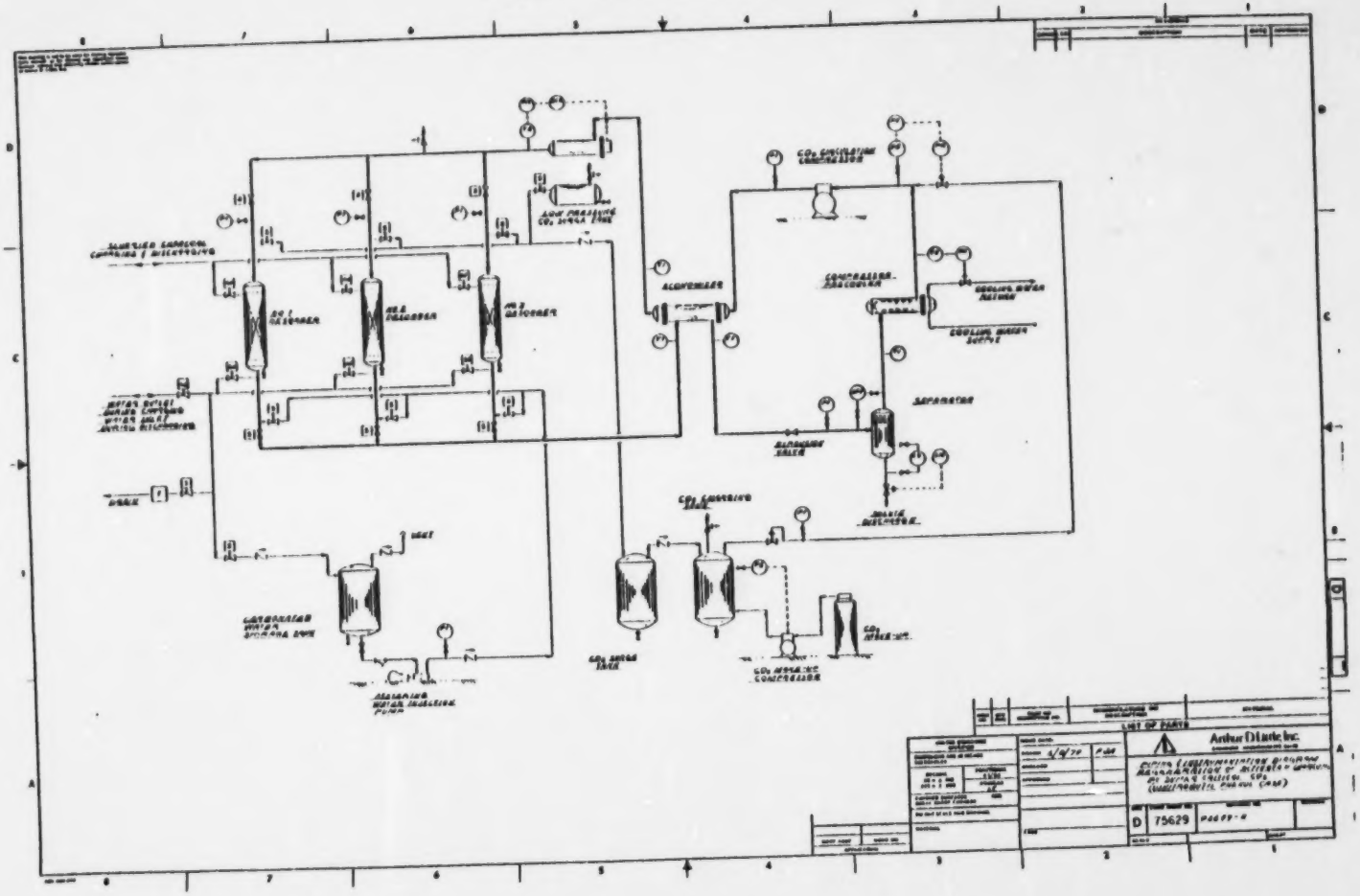
ii) GAC Charging and Discharging

Spent GAC is transferred from storage as a slurry to the available desorber. The desorber is equipped with a plate or screen assembly to hold the charged GAC and allow drainage of superficial water. It is assumed that no pore water is drained.

After regeneration is complete, GAC is discharged by up-flow of water, providing slurry flow of carbon to the adsorption columns.

The following equipment is off-plot and not included in the cost of the regeneration plant: spent GAC storage tanks; regenerated GAC storage tanks; slurry pump for charging; and high-water-flow carbon discharge pump.

FIGURE V-7
DNBP GAC REGENERATION SYSTEM
PIPING AND INSTRUMENTATION DIAGRAM



iii) Transfer of CO_2 Between Columns

The regeneration plant operates with one desorber on stream (for CO_2 circulation), and two desorbers involved in either charging or discharging carbon, or transferring CO_2 between them.

After a 30-minute regeneration cycle is completed in No. 1 desorber, flow is switched from No. 1 to No. 2 desorber. No. 3 desorber has been charged with spent carbon, and is completely filled with water to minimize introduction of air into the system. The high-pressure metering water pump then transfers carbonated water into No. 1 desorber at a low flow rate (sufficiently low to keep the bed from partly fluidizing), and slightly above bed pressure. The high-pressure water flow displaces CO_2 from desorber No. 1 to desorber No. 3, thereby pressurizing No. 3 bed to desorption pressure, and displacing its interstitial water. No. 3 desorber is then ready to accept CO_2 circulation for regeneration.

No. 1 bed, containing regenerated GAC in high-pressure water, and with pores containing high-pressure CO_2, is let down to separator pressure and held to allow expansion and release of a portion of the pore-volume CO_2. That CO_2 is collected in a low-pressure surge tank. No. 1 bed is then vented to atmospheric pressure, and the regenerated carbon is discharged as described above.

The same transfer and venting operation takes place at the completion of regeneration in each of the beds in sequence. Automatic valve operation is anticipated and accounted for in instrumenting the plant.

iv) CO_2 Make-Up

CO_2 make-up is provided by cylinder liquid CO_2 at ambient temperature (or below) and its vapor pressure. A CO_2 charging tank is maintained at a pressure slightly above the compressor suction pressure. The charging tank is maintained full by flow from the low-pressure surge tank, and on demand by pressure control with flow from the make-up source.

Make-up to the circulation loop is based on flow control at the compressor suction. A short-fall on recycle flow will open the make-up valve to allow CO_2 to be drawn from the make-up CO_2 charging tank.

c. Process Costs

Table V-5 lists the individual equipment components for the 2000 lb/day plant. For most components, the specification given resulted from discussions with suppliers and identification of specific hardware. Estimates of total system cost were made from summing the component costs, determining assembly costs from structure and piping layout sketches, and using accepted installation factors.

Operating costs, including capital depreciation, are summarized in Table V-6. At this small capacity, capital-related and labor-related costs are dominant; they represent 90% of total processing cost of $0.29/lb. Energy cost is 2.5¢/lb, which is 8.5% of the total.

B. Atrazine Wastewater

1. Introduction

In 1979, a preliminary experimental study was carried out with a wastewater sample from production of atrazine. The results were presented in a previous report (2). In this program, additional experimental data were obtained for SCF CO_2 regeneration with a second wastewater sample, and these data were used as the basis of an engineering and economic evaluation of the process with activated carbon.

Atrazine is a triazine compound, used to control weeds in corn, sorghum and sugarcane fields. The compound, commercially available for more than twenty years, is nonflammable, noncorrosive, and highly stable. Atrazine is relatively nontoxic with an LD_{50} for rats of 3080 mg/kg with no reported cases of ill effects to humans. The compound is synthesized by reacting cyanuric chloride with ethylamine and isopropylamine, in the presence of an acid.

TABLE V-5

REGENERATION OF ACTIVATED CARBON BY SUPERCRITICAL CARBON DIOXIDE: LIST OF MAJOR COMPONENTS

DNBP CASE: 2000 LBS/DAY GAC

1.	Desorber Assembly	- 3 (14" OD x 50" L) made from C/S A105 forgings. Bored to have thickness = 2.37", lined with 1/8" S.S. 304, interconnected with 1/2" S.S. 304 piping. Mounted with required valves and instruments.
2.	Carbonated Water Storage Tank	- Carbon steel, 150 # design, 30 gal.
3.	Metering Water Injection Pump	- 5 GPM, 14.7 # to 4000 # Wheatley, plunger pump, 5000 # design, carbon steel construction. 2000 RPM, 20 HP, 20" x 30" base plate, 2-1/2" piping
4.	Low Pressure CO_2 Surge Tank	- 10 ft^3, 500 # design, S.S. 304
5.	High Pressure CO_2 Surge Tank	- 14" OD x 50" L, 2500 # design, carbon steel
6.	CO_2 Charging Tank	- 14" OD x 50" L, 2500 # design, carbon steel
7.	Economizer	- Shell and tube heat exchanger, BEM 45 ft^2, all stainless steel construction Design pressure: tube side = 4500 #, shell side = 1500 #
8.	Separator	- Cyclonic type, S.S. 304
9.	Compressor Precooler	- 12 ft^2, Graham Heliflow CO_2 in tube side, cooling water in shell side S.S. 304 for tubes, carbon steel for shell
10.	Circulation Compressor	- Diaphragm type, .7 ft^3/min. displacement, 25 HP, PPI
11.	Heater	- Electric resistance type, Haynes, incoloy sheathed elements with Hi-temp cut-out, 12 KW

TABLE V-6

ESTIMATED PROCESSING COST* OF ACTIVATED CARBON REGENERATION BY SUPERCRITICAL CARBON DIOXIDE PROCESS

Plant Capacity: 2,000 lbs/day Regenerated Charcoal
Case: DNBP
Operating Factor: 330 days/yr
Capital Investment: $520,300

Variable Costs	Unit/Day	$/Unit	$/Day
Electricity	1009 KWH	0.05	50.45
Cooling Water	14.4 MGal	0.10	1.44
Make-up CO_2	200 Lbs	0.04	8.00
			59.89

Semivariable Costs	
Operating Labor: 1/2 man/shift, 3 shifts/day @ $10/hr	120.00
Supervision: 1/2 man @ $20,000/yr	30.30
Labor Overhead: 40% Labor & Supervision	60.12
Maintenance: 2% of Capital Investment/yr	31.53
	241.95

Fixed Costs	
Plant Overhead: 60% of Labor & Supervision	90.18
Taxes & Insurance: 1.5% of Capital Investment/yr	23.65
Depreciation: 10% of Capital Investment/yr	157.67
	271.50

573.34

Direct Processing Costs: $573.34/day

$ 0.29/lb of Regenerated Carbon

*mid-1980

A characterization of the wastewater from this process is shown in Table V-7. It can be seen that atrazine contributes only 10% of the total organic carbon (TOC) present in the wastewater. Other possible organics listed include the starting materials used to manufacture the herbicide as well as other reaction products.

2. Experimental Study

The study consisted of multi-cycle adsorptions and regenerations of a carbon column at a particular set of temperature and pressure conditions. By continually monitoring the weight adsorbed and desorbed during the cycles, one can determine the "steady state" working capacity of the carbon. Four separate multiple-cycle tests were carried out, each at a different set of conditions, to determine the sensitivity of working capacity to regeneration temperature or pressure.

The adsorption apparatus used is identical to the one described in Section VA (Figure V-1). Filtered atrazine wastewater was pumped upflow through GAC columns at 3.2 ml/min (1.1 GPM/ft^2). The effluent from the carbon column passed through a UV spectrophotometer set to 270 nm. UV scans of column effluent were used to track relative concentration as adsorption breakthrough occurred. After each adsorption, the GAC columns were backwashed, dried and weighed to determine the actual weight picked up.

The regeneration apparatus and procedures also were identical to that described in Section VA (Figure V-3). The extent of regeneration was determined by direct weighing of the GAC columns before and after desorption.

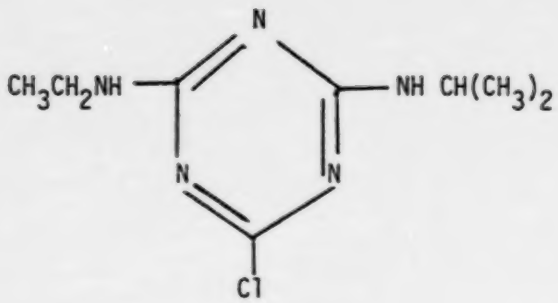
The four regeneration conditions tested were:

ATR-1: 120°C, 150 atm
ATR-2: 120°C, 275 atm
ATR-3: 220°C, 275 atm
ATR-4: 220°C, 150 atm

TABLE V-7

ATRAZINE CHARACTERISTICS

1. Molecular Structure:



2. Wastewater Concentrations (Approximate):

TOC	1000 ppm
Atrazine	100 ppm

3. Other Possible Components of Wastewater:

Sodium Chloride	NaCl
Cyanuric Chloride	$C_3N_3Cl_3$
Ethylamine	$C_2H_5NH_2$
Isopropylamine	$(CH_3)_2$ CH NH_2

The results of the four tests were as follows:

ATR-1: (120°C, 150 atm). This series was aborted during its third regeneration due to a compressor failure. The amount desorbed fell to a value of 0.03 gm/gm or below after the second cycle, and the series was not restarted. An extrapolation of the data would give a steady state capacity of about 0.02 gm/gm (Table V-8).

ATR-2: (120°C, 275 atm). This series, conducted at a higher pressure, was carried out for five complete cycles. As seen in Table V-9, the amount adsorbed and desorbed after five cycles appears to be converging at about 0.05 gm/gm.

ATR-3: (220°C, 275 atm). This series combined both high temperature and high pressure during regeneration. However, the steady state working capacity stayed at about 0.05 gm/gm (Table V-10). During the fourth cycle, the loading increased to 0.31 gm/gm. Since it decreased in the next cycle, it was hypothesized that the column was weighed while it still held some water in the pores, although every effort was made to dry and cool the column before weighing.

ATR-4: (220°C, 150 atm). This series was run at the lower operating pressure, but the higher temperature. It appears that the regeneration efficiency was not as high as when performed at high pressures. From Table V-11, the steady state capacity is about 0.04 gm/gm.

The results of this study showed that a steady state working capacity of 0.04 gm/gm can be achieved at either an elevated temperature or an elevated pressure, but that the combination of high temperature and pressure does not bring any increased regeneration efficiency.

It is important to note that this capacity is 10-15% of that of virgin carbon. The practical competitiveness of SCF CO_2 regeneration is linked to the working capacities achievable using thermal methods. A complete evaluation of this or any other specific application requires comparable data for working capacity after multiple cycles of thermal regeneration.

TABLE V-8

ATRAZINE WASTEWATER SERIES

Column ATR-1

Conditions:

Adsorption Flowrate: 3.2 ml/min (1.1 GPM/ft^2)

Regeneration CO_2 Flow: 120°C, 150 atm, 10-15 standard liters/min

Initial Carbon Weight: 7.0 gm

Loading (gm/gm GAC)

Cycle #	After Adsorption	After Regeneration	Adsorbed This Cycle	Desorbed This Cycle
1	0.33	0.29	0.33	0.04
2	0.36	0.33	0.07	0.03
3	0.39	-	0.06	-

TABLE V-9

ATRAZINE WASTEWATER SERIES

Column ATR-2

Conditions:

Adsorption Flowrate: 3.2 ml/min (1.1 GPM/ft^2)

Regeneration CO_2 Flow: 120°C, 275 atm, 10-15 standard liters/min

Initial Carbon Weight: 7.0 gm

Loading (gm/gm GAC)

Cycle #	After Adsorption	After Regeneration	Adsorbed This Cycle	Desorbed This Cycle
1	0.35	0.28	0.35	0.07
2	0.41	0.34	0.13	0.07
3	0.43	0.36	0.09	0.07
4	0.44	0.39	0.08	0.05
5	0.45	0.40	0.06	0.05

TABLE V-10

ATRAZINE WASTEWATER SERIES

Column ATR-3

Conditions:

Adsorption Flowrate: 3.2 ml/min (1.1 GPM/ft^2)

Regeneration CO_2 Flow: 220°C, 275 atm, 10-15 standard liters/min

Initial Carbon Weight: 7.0 gms

Loading (gm/gm GAC)

Cycle #	After Adsorption	After Regeneration	Adsorbed This Cycle	Desorbed This Cycle
1	0.29	0.20	0.29	0.09
2	0.32	0.25	0.12	0.07
3	0.33	0.29	0.08	0.04
4	0.60*	0.31	0.31*	0.29*
5	0.36	0.32	0.05	0.04

*Probably in error due to inadequate drying before weighing.

TABLE V-11

ATRAZINE WASTEWATER SERIES

Column ATR-4

Conditions:

Adsorption Flowrate: 3.2 ml/min (1.1 GPM/ft^2)

Regeneration CO_2 Flow: 220°C, 150 atm, 10-15 standard liters/min

Initial Carbon Weight: 7.0 gsm

Loading (gm/gm GAC)

Cycle #	After Adsorption	After Regeneration	Adsorbed This Cycle	Desorbed This Cycle
1	0.27	0.21	0.27	0.06
2	0.31	0.27	0.10	0.04
3	0.33	0.29	0.06	0.04
4	0.34	0.31	0.05	0.03
5	0.36	0.32	0.05	0.04
6	0.36	0.32	0.04	0.04

3. Engineering and Economic Evaluation

For the engineering and economic evaluation, conditions of 150 atm and 220°C were selected. The treatability studies indicated that working capacity was 0.04 gms/gm GAC under these conditions. Because pressure has a stronger negative influence on costs than temperature, the lower-pressure, higher-temperature combination giving this capacity was chosen.

Separator conditions of 40°C and 80 atm were used. This pressure is lower than the level of 120 atm selected for the DNBP case described in Section VA. For the atrazine case, it was desirable to assure that high purities were obtained in the recycled CO_2. CO_2 flow was derived from the same bases given for DNBP in Section VA. Knowing the manufacturer's wastewater flow and atrazine load in the wastewater, 5000 lbs per day of carbon use was calculated as the regeneration capacity required.

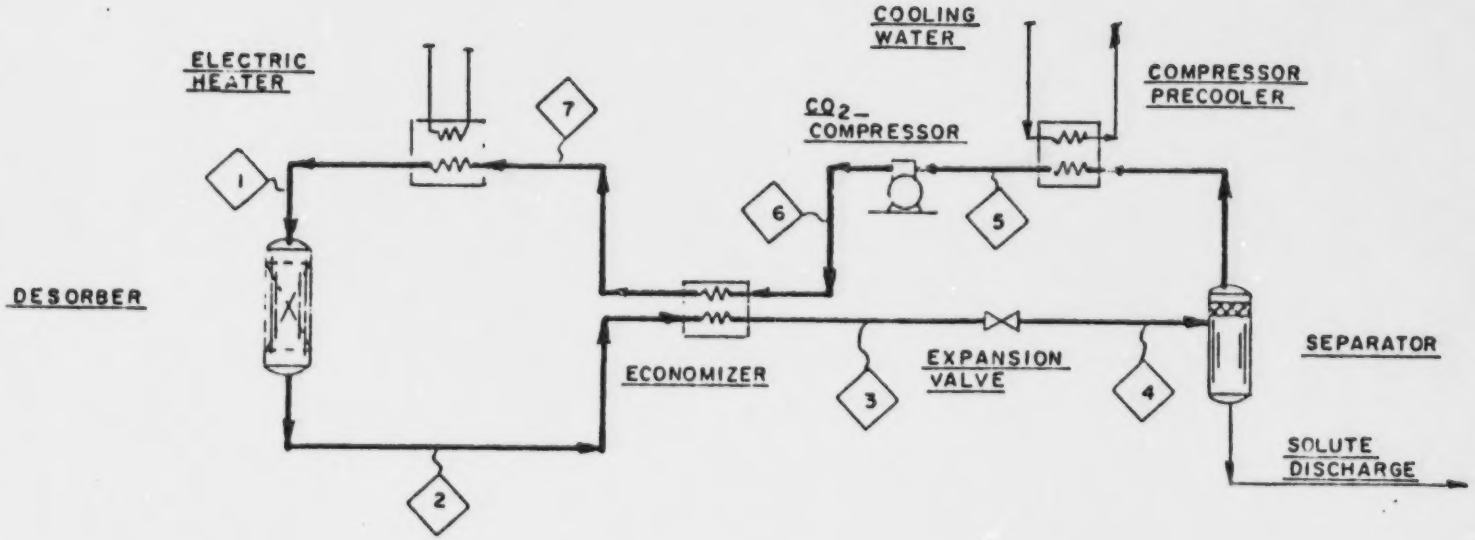
An overall process flow is shown in Figure V-8, and the total processing costs are shown in Table V-12.

Comparison of these results with thermal regeneration or use of contract service carbon both would require knowledge of working capacities in each case. If working capacities were comparable to that of SCF CO_2-regenerated carbon, however, the CO_2 process would appear quite favorable: thermal regeneration costs are about $0.20-0.30 per pound of carbon (3), and service carbon costs are in excess of $0.45 per pound, according to the atrazine manufacturer.

C. Chemical Plant Wastewater

In October, 1979, discussions were held with a South Carolina manufacturer of chemicals concerning possible treatability of a combined industrial wastewater using activated carbon and SCF CO_2 regeneration. A thermal regeneration system was under consideration for carbon used to treat this and other wastewaters in nearby plants, but both operating and capital costs were considered to be high.

FIGURE V-8



STATE POINT	1	2	3	4	5	6	7
LOCATION	DESORBER INLET	ECONOMIZER INLET	EXPANSION VALVE INLET	SEPARATOR INLET	COMPRESSOR INLET	COMPRESSOR OUTLET	ELECTRIC HEATER INLET
CO_2 FLOW RATE LB/HR	5,000	5,000	5,000	5,000	5,000	5,000	5,000
PRESSURE PSIA (BAR)	2250 (155)	2250 (155)	2250 (155)	1160 (80)	1160 (80)	2250 (155)	2250 (155)
TEMPERATURE °F (°C)	428 (220)	428 (220)	166 (74.4)	104 (40)	90 (322)	140 (60)	380 (193)

PROCESS FLOW DIAGRAM
REGENERATION OF ACTIVATED CHARCOAL
BY SUPER CRITICAL CARBON DIOXIDE
ATRAZINE CASE

TABLE V-12

ESTIMATED PROCESSING COST* OF ACTIVATED CARBON REGENERATION BY SUPERCRITICAL CARBON DIOXIDIE PROCESS

Plant Capacity: 5,000 Lbs/day Regenerated Carbon
Case: Atrazine
Operating Factor: 330 days/yr
Capital Investment: $600,000

Variable Costs	Unit/Day	$/Unit	$/Day
Electricity	2522.5 KWH	0.05	$126.13
Cooling Water	36 MGal	0.10	3.60
CO_2	500 Lbs	0.04	20.00
			149.73
Semivariable Costs			
Operating Labor: 1/2 man/shift, 3 shifts/day @		$10/hr	120.00
Supervision: 1/2 man @ $20,000/yr			30.30
Labor Overhead: 40% Labor & Supervision			60.12
Maintenance: 2% of Capital Investment/yr			36.36
			246.78
Fixed Costs			
Plant Overhead: 60% of Labor & Supervision			90.18
Taxes & Insurance: 1.5% of Capital Investment/yr			27.27
Depreciation: 10% of Capital Investment/yr			181.82
			299.27

Direct Processing Costs: $695.78/Day

$ 0.14/Lb of Regenerated Carbon

*mid-1980

A sample of the South Carolina wastewater was obtained and a series of tests were run to determine treatability. While a complete experimental and economic evaluation was not performed, the preliminary results are reported herein.

An initial attempt was made to develop an ultraviolet-based spectroscopic analysis of the wastewater organics. A feed sample was traced over the UV range of 200-320 nm, as were effluent samples taken at various points during breakthrough from the carbon bed. It was concluded that there were insufficient distinctions among the UV adsorbance to provide good quantitative data. As a result, analyses were performed using total organic carbon (TOC).

The regeneration tests consisted of an initial adsorption test on fresh carbon, followed by a single regeneration at selected conditions, and then a second adsorption to provide the estimate of working capacity. These results are summarized in Table V-13.

Regeneration at 150°C and 157 atm produced a working capacity of 0.03 lbs/lb. An increase in temperature to 225°C caused a doubling of capacity to 0.06 lbs/lb. Increased pressure to 307 atm (at 200°C) provided another doubling of capacity, to 0.13 lb/lb. Directionally, both effects were similar to those observed with the DNBP wastewater described previously.

TABLE V-13

RESULTS OF INITIAL SCREENING WITH SCF/CO_2:
CHEMICAL-PLANT WASTEWATER

Regeneration Conditions		Estimated Multicycle Working Capacity
Temp (^{o}C)	Pressure (atm)	lb/lb GAC
150	157	0.03
225	157	0.06
200	307	0.13

VI. SYNTHETIC RESIN ADSORPTION-REGENERATION STUDIES

A. Introduction

The major factor constraining expanded use of adsorbents in wastewater treatment has been cost, and much of that cost is associated with adsorbent regeneration for reuse. Existing thermal regeneration processes are capital and energy intensive. Solvent regeneration processes are expensive because of the requirements for removal of solvents from adsorbents and for purifying spent solvents for recycle.

In this work and prior studies (2), results have been reported for regeneration of activated carbon using supercritical carbon dioxide as a desorbent. The objective of the work described in this section was to compare supercritical fluid regeneration of four selected resinous adsorbents with activated carbon. Adsorbates were selected to represent a range of molecular weights, solubility in water, and polarity. Supercritical carbon dioxide regeneration costs were estimated to compare the use of resinous adsorbents with activated carbon for the removal and recovery of phenol and alachlor.

In recent years, polymeric resinous adsorbents and carbonaceous resinous adsorbents have been developed and have proven useful in numerous applications. In resin adsorption processes, adsorbent regeneration (solute desorption) and reuse are usually required for favorable operating economics. The most widely used regeneration method for activated carbons is high-temperature thermal processing.

Since high-temperature regeneration would destroy polymeric and carbonaceous resinous adsorbents, solvent elution is required for desorption of adsorbed materials. Water or water-soluble solvents (such as 2-butanone, 2-propanone, 1-butanol, 1-propanol, ethanol or methanol) are normally used (4, 5). Due to the cost of solvents, operating cost economy usually dictates that solvent recovery techniques be employed. Such techniques

normally employ distillation equipment to separate desorbed compounds from the spent desorbent solvent. As the solvent is introduced, the process liquid must be displaced from the adsorbent and, following the desorption step, solvent must be displaced by the process liquid. This results in a solvent stream which is contaminated with both desorbed components and the process liquid. This situation becomes more complicated if the solvent required is not miscible with the process liquid. Formation of azeotropic mixtures of solvent in the process liquid often occurs.

It is known that many materials (solutes) become substantially more soluble in normally gaseous solvents near or above their critical points. Solute solubility in the supercritical fluid is often very dependent on temperature and pressure. This property provides a useful means of desorbing molecular species from a solid adsorbent material and later separating these solutes from the desorbent solvent by changing temperature and pressure conditions. Both the solute and the solvent may be recovered in this manner. Thus, supercritical fluids as desorbents for solid adsorbents offer the advantage of solute recovery as well as lower energy requirements. The possibility exists for separate recovery of individual solutes from a mixture of solutes by progressive adjustments in temperature and pressure (6).

B. Experimental Details

1. Characteristics of Synthetic Adsorbents

A number of synthetic adsorbents are available today which offer the potential end user the ability to select an adsorbent best suited for the desired separation. These synthetic adsorbents offer a range of size distributions and surface characteristics. The manufacturing methods employed to produce synthetic adsorbents allow good control over the pore size distribution. Typically, the production of activated carbons lacks this close control of pore size distribution and produces a more heterogeneous surface structure. The well-defined structure of synthetic adsorbents often allows selection of an adsorbent that optimizes efficiency

of adsorption and ease of desorption or allows selective adsorption of a specific component from a mixture.

Five adsorbents were chosen for this study: two adsorbents were polymeric resinous adsorbents and two adsorbents were carbonaceous resinous adsorbents. The fifth adsorbent was a commonly used activated carbon. Physical properties are summarized in Table VI-1. Pore-size distributions are shown in Table VI-2.

The two polymeric resinous adsorbents studied were Rohm & Haas XAD-4 and Diamond Shamrock ES-865. These polymeric resinous adsorbents are nonpolar macroporous copolymers of styrene and divinylbenzene. They are produced by suspension polymerization of a monomer, such as styrene, and a cross-linking agent, such as divinylbenzene. The polymerization is achieved in a solvent which is able to dissolve the monomers, but which is a poor swelling agent for the forming cross-linked polymer. In time, a phase separation takes place resulting in polymer beads which contain microscopic gel structures. The gel structures are joined at points of contact thus producing interconnecting pores which, along with the polymers, are present as continuous phases. The average pore size and surface area of the formed copolymer are a direct result of this internal gel structure and can be controlled by the types and amounts of monomers and solvents used in the polymerization process. A wide range of surface area, pore size and pore volume can be developed in this type of adsorbent with the added benefits of well-defined surface characteristics (4).

The two carbonaceous resinous adsorbents studied were Rohm & Haas XE-340 and XE-348. The carbonaceous resinous adsorbents are produced by partial pyrolysis of a synthetic copolymer. The pore-size distribution is determined by the starting copolymers and the maximum porosity in a desired diameter range can be controlled by the degree of pyrolysis (7).

The polymeric and carbonaceous resinous adsorbents do not have the broad spectrum adsorptive capabilities of activated carbon; however, greater

TABLE VI-1

ADSORBENT PHYSICAL PROPERTIES

PROPERTIES	XAD-4	ES-865	XE-340	XE-348	Filtrasorb 300 (Granular Activated Carbon)
PARTICLE SIZE, U.S. SCREEN MESH RANGE	20-60	20-50	20-50	20-50	8-30
BULK DENSITY, g/cm^3	0.63	0.63	0.59	0.59	0.49
SKELETAL DENSITY, g/cm^3	1.08	1.08	1.34	1.95	2.10
PORE VOLUME, cm^3/g	0.99	1.40	0.34	0.58	0.85
SURFACE AREA, m^2/g	725	700	400	500	950-1050

TABLE VI-2

ADSORBENT PORE-SIZE DISTRIBUTION
PERCENT OF TOTAL PORE VOLUME

PORE SIZE	XAD-4	ES-865	XE-340	XE-348	Filtrasorb 300 (Granular Activated Carbon)
<6	—	—	0	16	4
6-40	6	10	18	21	41
40-100	16	15	13	9	5
100-300	28	25	69	51	9
> 300	50	50	0	3	41

capacities for certain solute species which match the synthetic adsorbent's porosity and polarity are generally achieved. In general, polymeric resinous adsorbents contain a narrow distribution of relatively large pores. The carbonaceous adsorbents have a narrow pore distribution as do the polymeric adsorbents, but the pore size is generally in a smaller range. When compared to polymeric adsorbents, activated carbons contain a wide pore-size distribution with a substantial amount of porosity in the 5-20 Angstrom range (7).

While it is not possible to accurately predict which materials will be adsorbed well by a given adsorbent, certain mechanisms can be postulated. Generally, hydrophobic or nonpolar molecules or portions of molecules are attracted to hydrophobic surfaces, and hydrophilic or polar molecules are attracted to hydrophilic or polar surfaces. If one thinks of each organic molecule as having both a hydrophobic and hydrophilic end, then the hydrophobic end will be attracted to adsorbents such as Amberlite XAD-4 and Duolite ES-865. This is particularly true when the adsorption takes place from an aqueous solution (8).

The carbonaceous adsorbent Ambersorb XE-340 is hydrophobic in nature and is especially suited for removal of low molecular-weight halogenated hydrocarbons from water. Ambersorb XE-348 is a broad spectrum adsorbent when compared to XE-340 and is more similar to activated carbon. Ambersorb XE-348 is effective in removal of more polar organics, such as phenol (9).

The surfaces of the polymeric adsorbents such as XAD-4 and ES-865 have no ionic functionality and thus the binding energies of these adsorbents are lower than those of activated carbons or the carbonaceous adsorbents. These low binding energies contribute to their ease of regeneration or desorption.

2. Adsorbates or Solute Chemicals

For this work, acetic acid, phenol and alachlor were selected to represent a range of molecular weights, solubility in water, and polarity.

Several generalizations can be useful in characterizing the adsorptivity of organics by common low-polarity solid adsorbents:

a. Adsorption of organics increases with increasing molecular weight, until molecular size exceeds the adsorbent pore size.
b. Adsorption increases with decreasing water solubility.
c. Nonpolar organics are much more strongly adsorbed from water than are polar organics.

Other factors, such as temperature, pH, and the presence of competing solutes may also influence adsorptivity (10).

As indicated in Table VI-3, acetic acid is very polar, has infinite water solubility and has a low molecular weight. Alachlor by comparison is only slightly polar, has a low water solubility and has a high molecular weight. Phenol is intermediate between acetic acid and alachlor with respect to polarity, solubility and molecular weight.

Adsorption of these chemicals had previously been studied on Calgon F-300 granular activated carbon (2).

3. Experimental Procedures

a. Preconditioning of Adsorbents

Prior to use as adsorbents, the XAD-4 and ES-865 polymeric resinous adsorbents were preconditioned by washing with methanol in a Buchner funnel using a slight vacuum to draw the methanol wash solution through the adsorbent. After washing with methanol, the adsorbents were rinsed with deionized water, evacuated of interstitial water, oven dried at 100°C, and stored in a dessicator.

The Ambersorb carbonaceous resinous adsorbents were oven dried at 100°C and stored in a dessicator. Approximately 7 grams (dry weight) of each adsorbent were weighed, rehydrated using a methanol-water solution, placed in a 15 mm i.d. by 150 mm chromatography column and rinsed with approximately one liter of deionized water prior to the adsorption cycle.

TABLE VI-3

SOLUTE PHYSICAL DATA

SOLUTE	POLARITY	MOLECULAR WEIGHT	AQUEOUS SOLUBILITY
ALACHLOR	SLIGHTLY POLAR	269.45	0.12 g/l
PHENOL	POLAR	94.1	82 g/l
ACETIC ACID	VERY POLAR	60.5	∞

b. Adsorption

Aqueous solutions of solute were gravity fed to the adsorbent columns at ambient temperature. The flow rate was controlled with an effluent valve. Composite effluent samples were collected sequentially from each column and analyzed for solute concentration. The phenol and alachlor analyses were performed by gas chromatography. The acetic acid analysis was performed by liquid chromatography.

Adsorption of the solute was continued until the adsorbent column effluent concentration was 90-100% of the influent concentration.

After the adsorbents were completely loaded with the solute, feed flow was stopped and the interstitial liquid was removed from the column using a vacuum source. The adsorbents were then dried in their respective chromatography tubes with low pressure nitrogen at 50-60°C.

After drying, the adsorbents were quantitatively removed from their columns and weighed. The weight of the solute adsorbed was determined by adsorbent weight gain. As a verification, the adsorbent weight gain was compared to the solute removed from the feed, as determined by integration of the column breakthrough curves. Agreement between the two methods was within expected experimental error.

c. Desorption by Supercritical Carbon Dioxide

The bench-scale apparatus, used for supercritical fluid desorption of solutes previously loaded onto solid adsorbents was the same as that shown in Figure V-3. Prior to desorption, each adsorbent (dried) was transferred to a high-pressure 2.07-cm ID by 20.3-cm long stainless-steel column. Liquid carbon dioxide (siphon grade, minimum 99.5% purity) was pumped to the required operating pressure using an Aminco Model 46-13427 diaphragm compressor, raised to the required operating temperature in a preheater, passed through the desorption column and out to a pressure let-down valve. The desorbed solute was collected in a U-tube cold trap which had been

preweighed. The rotameter downstream of the cold trap was used to indicate the instantaneous CO_2 volumetric flow rate. The total desorbent carbon dioxide usage was accumulated by a dry test gas meter.

During desorption, flow of the supercritical carbon dioxide was periodically interrupted. The U-tube was removed from the cold trap, weighed, replaced into the cold trap, and the amount of carbon dioxide flowed was recorded. Desorption was then continued. This procedure was repeated until no additional increase in the U-tube weight was observed, indicating that desorption of the solute from the solid adsorbent was complete.

C. Experimental Results

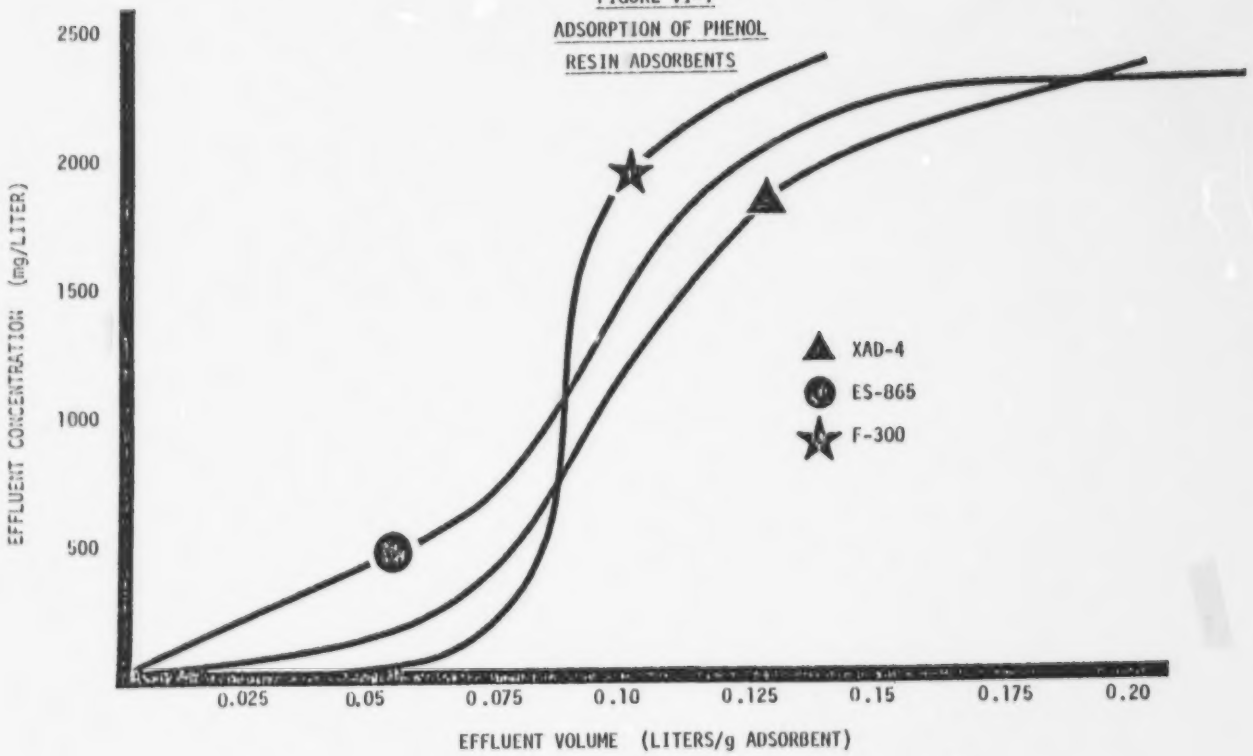
Adsorption and regeneration data for the two polymeric resinous adsorbents, two carbonaceous resinous adsorbents and one activated carbon adsorbent were developed and used to compare the desorptive characteristics of these adsorbents when used to treat phenol, alachlor and acetic acid. Tabulated data are presented in Appendix A.

Single-cycle adsorption and desorption tests were completed for each adsorbent with each solute; thus, long-term effects of incomplete solute desorption were not evaluated. It should be noted that extensive multi-cycle data for granular activated carbon (2) have shown that the major fractional loss in adsorbent working capacity occurs after the first cycle. Comparison of first-cycle desorption vs. adsorption gives a measure of capacity recovery after one cycle.

1. Phenol

Phenol adsorption was carried out using a solution of 2,200 mg/liter phenol in water at a flow of 3.2 ml/min (1.1 gpm/ft^2). The adsorption breakthrough curves F-300, ES-865 and XAD-4 are shown in Figure VI-1. Phenol breakthrough occurs first in the ES-865, second in the XAD-4 and

FIGURE VI-1
ADSORPTION OF PHENOL
RESIN ADSORBENTS



last in the F-300. The slope of the solute breakthrough curve is steeper for the F-300 granular activated carbon adsorbent than for the polymeric resinous adsorbents.

Breakthrough curves for XE-340 and XE-348 carbonaceous resins are shown in Figure VI-2, along with the F-300 breakthrough for comparison. Breakthrough for the carbonaceous adsorbents occurs prior to the activated carbon breakthrough, and the slopes of the carbonaceous-adsorbent breakthrough curves are less steep.

Phenol desorption of all the solid adsorbents was accomplished at 150 atm (2200 psig) and 55°C. The phenol concentration in the desorbent column effluent is shown for F-300, ES-865 and XAD-4 in Figure VI-3. The steeper slope of the desorption curves for the polymeric resin adsorbents indicates a more rapid desorption of phenol. Similarly, Figure VI-4 shows the desorption of phenol from the carbonaceous adsorbents XE-340 and XE-348 to be more rapid than the granular activated carbon adsorbent F-300.

Figure VI-5 displays the completeness of desorption as a function of the desorbent flowed. It should be noted that almost 100% solute desorption was achieved with the polymeric adsorbents, compared to substantially less-complete desorption achieved with the carbonaceous and granular activated carbon adsorbents. Also, the XE-348 adsorbent, which is reported to be most like granular activated carbon, showed a desorption profile very similar to that of granular activated carbon F-300.

The relative effectiveness of the supercritical CO_2 desorbent for each adsorbent is summarized in Table VI-4. Judging from the amount desorbed, the XAD-4 working capacity appears to be nearly the same as that for F-300, despite the high capacity of the virgin carbon. Indeed, the combined effects of phenol loading, rate of phenol desorption and completeness of desorption suggest that the polymeric adsorbent XAD-4 may be a viable alternative to F-300 granular activated carbon for phenol removal. Moreover, phenol can be desorbed from XAD-4 with substantially less carbon dioxide than that required for F-300.

FIGURE VI-2
ADSORPTION OF PHENOL
CARBONACEOUS ADSORBENTS

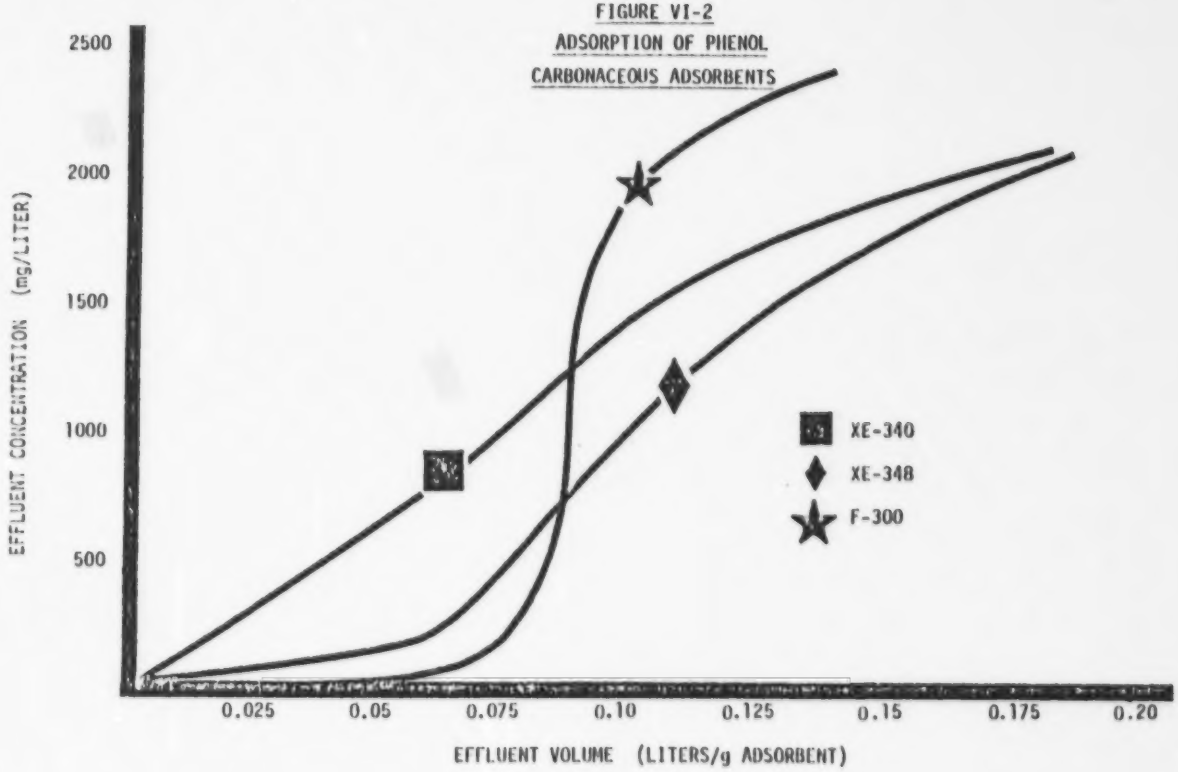


FIGURE VI-3
DESORPTION OF PHENOL:
EFFLUENT CONCENTRATIONS

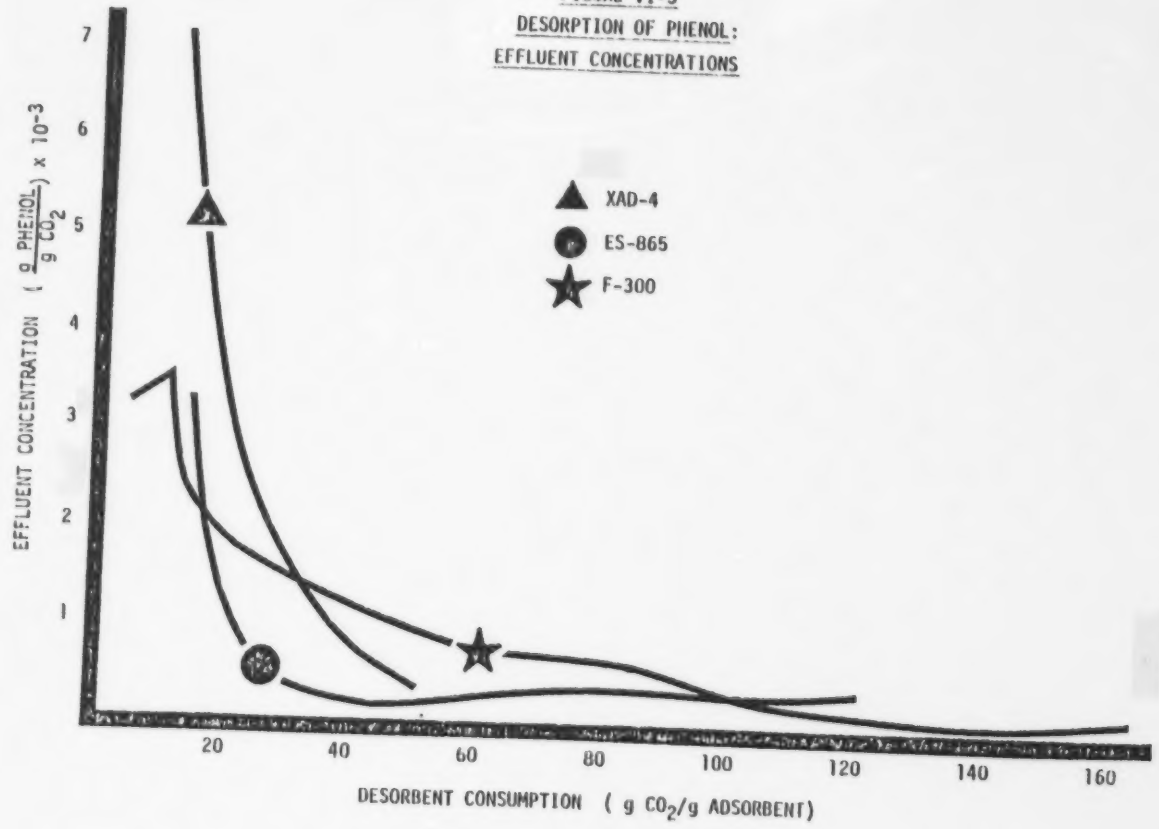


FIGURE VI-4
DESORPTION OF PHENOL:
EFFLUENT CONCENTRATIONS

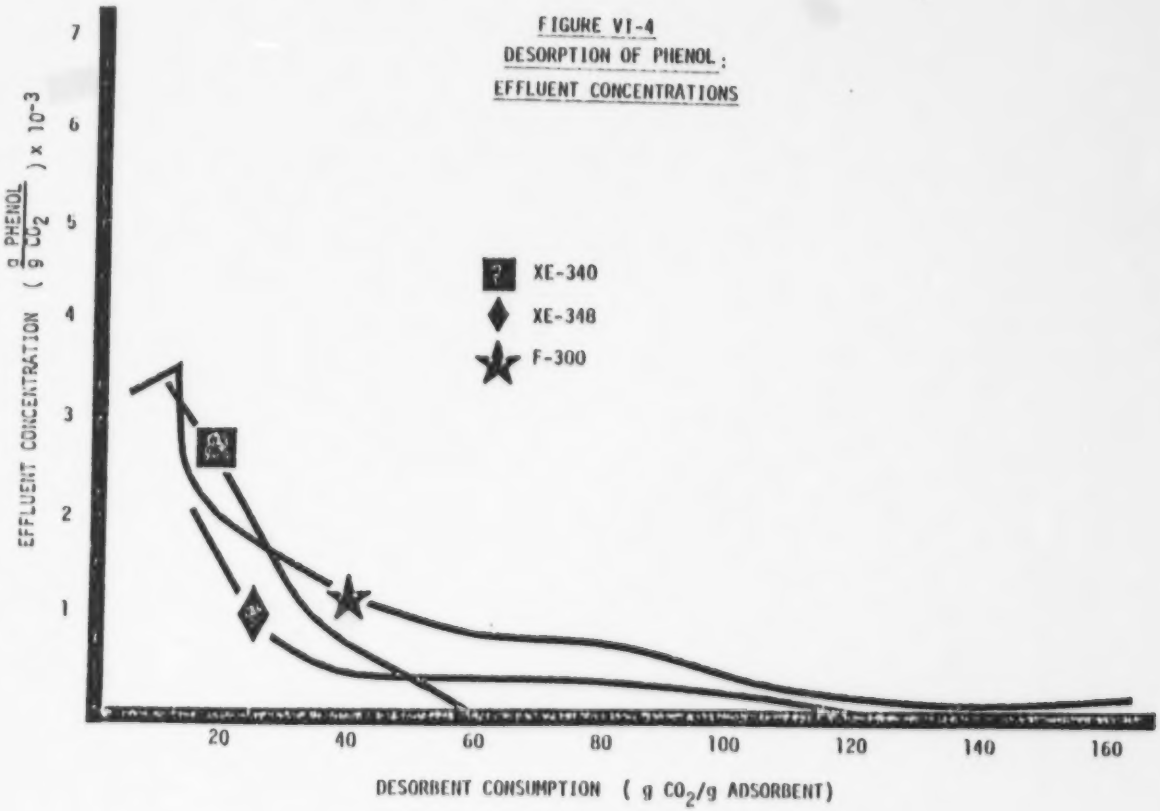


FIGURE VI-5
DESORPTION OF PHENOL
PERCENT DESORBED

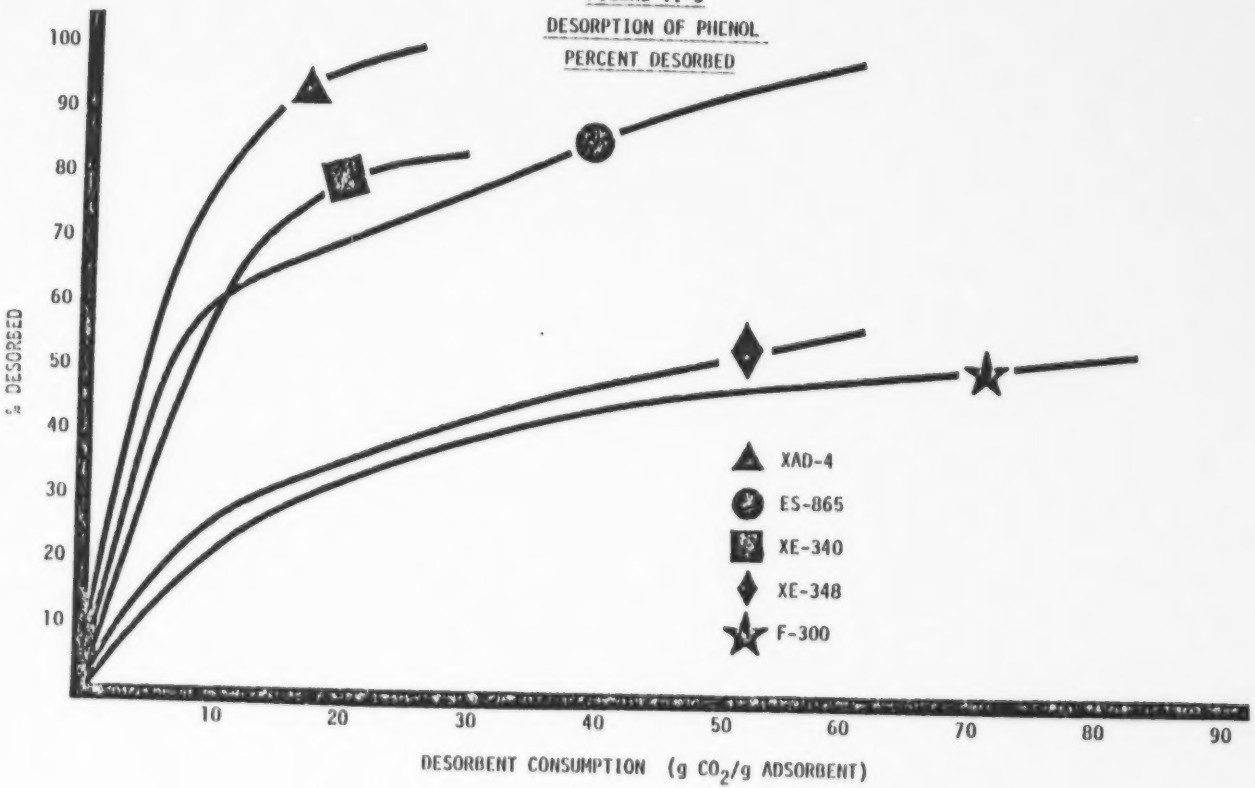


TABLE VI-4

PHENOL

ADSORBENT LOADING AND DESORPTION

ADSORBENT	LOADED g/g	DESORBED g/g	% DESORBED
XAD-4	0.14	0.14	100
ES-865	0.09	0.09	98.8
XE-340	0.10	0.08	83.0
XE-348	0.17	0.09	53.7
F-300	0.26	0.16	62.5

2. Alachlor

Alachlor adsorption onto the five adsorbents was accomplished with a solution of 120 mg/liter alachlor in water at a flow rate of 3.2 ml/min (1.1 gpm/ft^2). Breakthrough curves are shown in Figure VI-6. Breakthrough for F-300 and the carbonaceous resin adsorbents occurs well before those for the polymeric resin adsorbents.

Alachlor desorptions were run at 210 atm (3000 psig) and 55°C. The alachlor concentrations in the desorbent effluents are shown in Figure VI-7. The peak alachlor concentrations from the polymeric resins are very high relative to those from the carbonaceous and activated carbon adsorbents.

The desorption completeness as a function of the CO_2 flowed is displayed in Figure VI-8. Almost 100% solute desorption was achieved with the polymeric resinous adsorbents, while solute was poorly desorbed from the XE-348 and F-300. Previous data (2) indicated that more complete desorption of alachlor from activated carbon can be achieved at higher desorbent temperatures and pressures; however, in no case was 100% alachlor removal achieved.

The alachlor loading and desorption data is summarized in Table VI-5. It is evident that XAD-4 represents a very favorable alternative to F-300 for this solute. Virgin adsorbent capacity is three times as high, and that capacity is apparently maintained after regeneration. With F-300, however, only about 10% of the adsorbed alachlor is removed.

3. Acetic Acid

Acetic acid adsorption was carried out using a solution of 2400 mg/liter acetic acid in water at a flow rate of 3.2 ml/min (1.1 gpm/ft^2). The acetic acid breakthrough data was not plotted since solute breakthrough was rapid for all of the desorbents.

The acetic acid loading and desorption data is summarized in Table VI-6. Because of the low acetic acid loading levels on XAD-4 and ES-865, desorption

FIGURE VI-6
ADSORPTION OF ALACHLOR:
SYNTHETIC ADSORBENTS

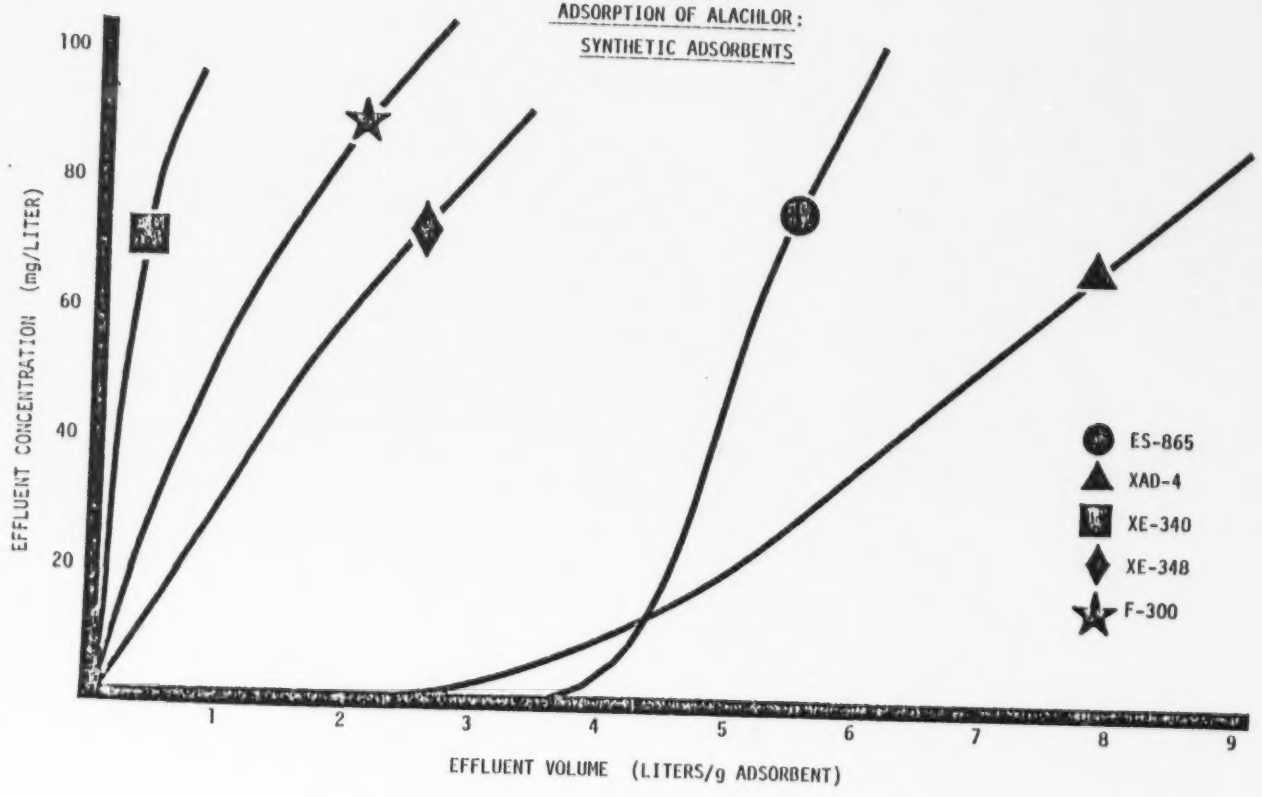


FIGURE VI-7
DESORPTION OF ALACHLOR:
EFFLUENT CONCENTRATIONS

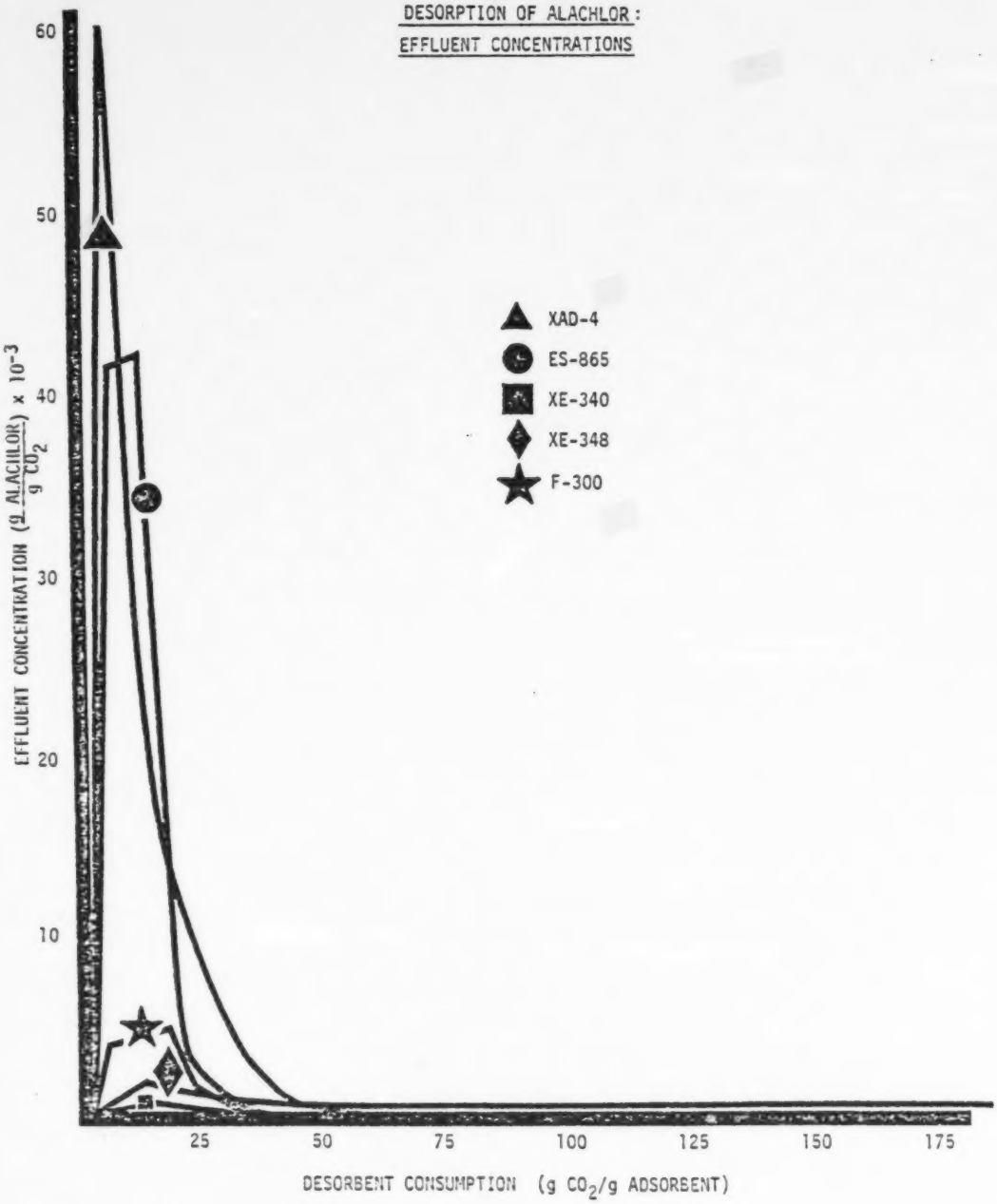


FIGURE VI-8
DESORPTION OF ALACHLOR:
PERCENT DESORPTION

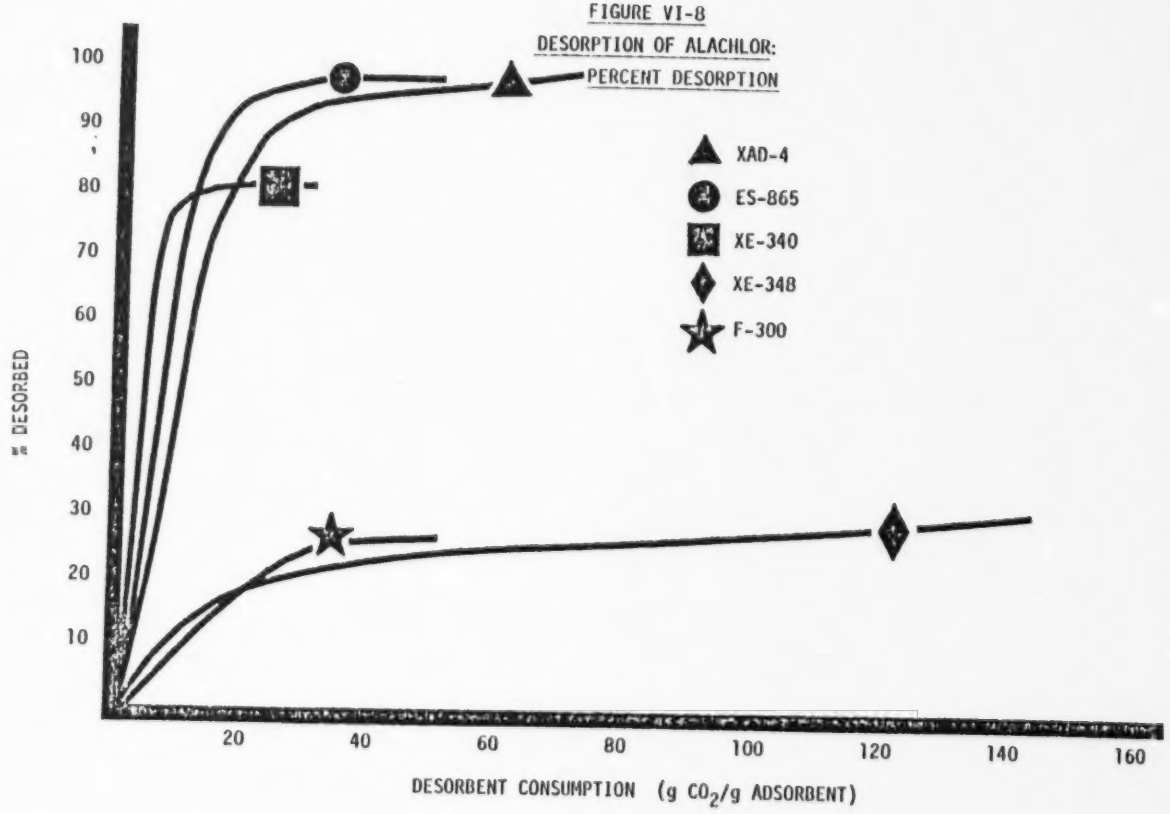


TABLE VI-5

ALACHLOR

ADSORBENT LOADING AND DESORPTION

ADSORBENT	LOADED g/g	DESORBED g/g	% DESORBED
XAD-4	0.63	0.62	99.2
ES-865	0.47	0.46	98.3
XE-340	0.03	0.02	77.8
XE-348	0.18	0.06	32.5
F-300	0.21	0.06	27.6

TABLE VI-6

ACETIC ACID

ADSORBENT LOADING AND DESORPTION

ADSORBENT	LOADED g/g	DESORBED g/g	% DESORBED
XAD-4	0.02	-	-
ES-865	0.02	-	-
XE-340	0.04	-	-
XE-348	0.08	0.08	100
F-300	0.05	0.05	100

of these adsorbents was not attempted. The highest loading was achieved with XE-348, 0.08 g/g.

Desorption of XE-348 and F-300 was done with carbon dioxide at 150 atm (2200 psig) and 25°C. Desorption of acetic acid from XE-348 and F-300 was rapid and complete. The data suggest that the carbonaceous adsorbent XE-348 may be a better adsorption alternative than F-300 carbon.

D. Regeneration Cost Considerations

The results presented herein provide a basis for a preliminary comparison of the relative energy economics for regenerating selected resin adsorbents and activated carbon with supercritical carbon dioxide.

The amount of solute desorbed from the virgin adsorbents can be used as a first approximation of long-term, steady-state working capacity; that is, subsequent adsorbent poisoning and fouling were considered to be negligible, and no decrease in operating capacity after the first cycle would occur with an adsorbent from which a solute is essentially completely desorbed. It has been demonstrated in other work that a decrease in capacity from that of the virgin adsorbent may occur after multiple adsorption-desorption cycles. However, generally the major decrease occurs in the first adsorption-desorption cycle. When a steady-state capacity is achieved, the solute desorbed will approximately equal the solute adsorbed.

The energy cost required to recompress the carbon dioxide from the adsorbate separator to the desorption pressure was estimated. Capital amortization, labor, adsorbent attrition, and other related costs were assumed to be comparable for each adsorbent; thus, energy costs would reflect the differences in processing costs.

A power cost of $0.05/kWh was used to calculate the compression cost. The conditions used were the following:

	DESORPTION CONDITIONS	SEPARATOR CONDITIONS	ENERGY COST PER kg CO_2
Phenol	Pressure = 150 atm (2200 psig) 55°C	80 atm (1176 psig) 35°C	$\$2.9 \times 10^{-4}$/kg CO_2
Alachlor	Pressure = 210 atm (3000 psig) 55°C	80 atm (1176 psig) 34°C	$\$4.1 \times 10^{-4}$/kg CO_2

The amount of carbon dioxide required to achieve essentially complete desorption was determined from Figure VI-5 for phenol, and from Figure VI-8 for alachlor; for each adsorbate, this gave kg CO_2/kg adsorbent for different adsorbents. The amount of adsorbent required to adsorb a given amount of adsorbate was determined from Table VI-4 for phenol and from Table VI-5 for alachlor; for each adsorbate, the reciprocal gave kg adsorbent/kg adsorbate. The product of multiplying (kg CO_2/kg adsorbent) by (kg adsorbent/kg adsorbate) gave the CO_2 requirement per unit of adsorbate (kg CO_2/kg adsorbate). Multiplying each by the energy cost per unit CO_2 gave the energy cost per unit adsorbate.

For phenol, the polymeric adsorbent XAD-4 was chosen for a comparison with F-300 because of the favorable desorption and phenol loading characteristics. Thus, for phenol with XAD-4, Figure VI-5 showed 95% desorption with 17 weights of solvent per weight of adsorbent. The compression energy per unit CO_2 was calculated to be 5.8×10^{-3} kwhr per kg CO_2, giving the energy cost of $\$2.9 \times 10^{-4}$/kg CO_2 shown above. For 17 kg CO_2 per kg adsorbent, the cost is \$0.005 per kg of adsorbent. For 0.10 kg phenol adsorbed per kg adsorbent (Table VI-4) the cost is \$0.05 per kg phenol. A similar calculation for phenol removed by F-300 gives a cost of \$0.17/kg of phenol. The cost saving is (0.17-0.05)/0.17 = 71%.

For alachlor desorption, both polymeric adsorbents XAD-4 and ES-865 displayed good loading and desorption characteristics. The F-300 activated carbon exhibited low capacity with high requirements for desorbent. The energy cost of alachlor desorption from the three adsorbents by supercritical carbon dioxide are as follows:

ADSORBENT	MAXIMUM DESORPTION POINT	ENERGY COSTS FOR DESORPTION, $/kg ALACHLOR
XAD-4	0.61 kg/kg	$0.04
ES-865	0.49 kg/kg	$0.05
F-300	0.06 kg/kg	$0.24

Thus, either XAD-4 or ES-865 are significantly more cost-effective for the removal and recovery of alachlor compared to F-300, based on compression requirements. The cost saving in this case is (0.24-0.04)/0.24 = 83%.

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APPENDIX A

RESIN ADSORPTION/DESORPTION TABULATED DATA

TABLE A-1

ADSORPTION OF PHENOL

XAD-4
7.74 gms adsorbent
2342 mg/l feed conc.

Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc, mg/l
0.065	298
0.129	1928
0.194	2302

ES-865
7.01 gms adsorbent
2205 mg/l feed conc.

Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc., mg/l
0.071	644
0.143	2176
0.214	2202

XE-348
Run 1
7.91 gms adsorbent
2239 mg/l feed conc.

Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc., mg/l
0.063	519
0.126	1635
0.189	1997
0.316	2200

Run 2
8.14 gms adsorbent
2100 mg/l feed conc.

0.061	220
0.123	1450
0.184	2035
0.246	2100

XE-340
Run 1
6.99 gms adsorbent
2239 mg/l feed conc.

Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc., mg/l
0.072	1225
0.143	1971
0.215	2213
0.286	2280

Run 2
8.43 gms adsorbent
2100 mg/l feed conc.

0.059	785
0.119	1690
0.178	2090

TABLE A-2

PHENOL DESORPTIONS: EFFLUENT CONCENTRATION PROFILES

F-300		XAD-4		ES-865		XE-340		XE-348	
gm CO_2 / gm adsorbent	Conc. phenol in wt fraction	gm CO_2 / gm adsorbent	Conc. phenol in wt fraction	gm CO_2 / gm adsorbent	Conc. phenol in wt fraction	gm CO_2 / gm adsorbent	Conc. phenol in wt fraction	gm CO_2 / gm adsorbent	Conc. phenol in wt fraction
5.68	3.29×10^{-3}	12.8	7.02×10^{-3}	15.0	3.37×10^{-3}	11.72	3.43×10^{-3}	17.28	2.18×10^{-3}
11.29	3.54	25.61	2.34	30.0	0.45	23.45	2.21	34.56	0.59
16.94	2.28	38.41	0.97	60.0	0.54	35.17	0.84	69.12	0.54
22.59	2.02	51.21	0.40	89.99	0.77	46.89	0.54	103.68	0.32
28.24	1.77			119.98	0.54	58.62	0.08	120.96	0.09
36.71	0.67								
48.01	1.11								
62.13	0.91								
76.25	0.81								
104.49	0.30								
115.78	0.20								
166.61	0.25								
214.62	0.15								
242.86	0.10								
273.93	0.14								
330.41	0.07								
386.89	0.05								
443.37	0.03								
511.14	0								

TABLE A-3

PHENOL DESORPTIONS: PERCENT DESORBED

F-300		XAD-4		ES-865		XE-340		XE-348	
gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed
5.68	7.1	12.8	65.6	15.0	58.8	11.72	40.2	17.28	22.6
11.29	14.8	25.61	87.5	30.0	66.7	23.45	66.1	34.56	34.8
16.94	19.8	38.41	96.5	60.0	76.0	35.17	75.9	69.12	46.13
22.59	24.2	51.21	100.2	89.99	89.46	46.89	82.1	103.68	52.76
28.24	28.0			119.98	98.8	58.62	83.0	120.96	53.7
36.71	30.2								
48.01	35.2								
62.13	40.1								
76.25	44.5								
104.49	47.8								
115.78	48.9								
166.61	53.8								
214.62	56.6								
242.86	57.7								
273.93	59.3								
330.41	61.0								
386.89	62.1								
443.37	62.6								
511.14	62.6								

TABLE A-4

ADSORPTION OF ALACHLOR

Feed Concentration: 105 mg/l

F-300 (7.03 gms)		XAD-4 (6.90 gms)		ES-865 (6.01 gms)		XE-340 (6.65 gms)		XE-348 (6.89 gms)	
Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc. mg/l	Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc. mg/l	Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc. mg/l	Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc. mg/l	Cum. Volume of Feed, Liters/Gm Adsorbent	Effluent Conc. mg/l
0.18	11	1.74	<1	3.30	<1	0.075	16.8	0.36	2.0
0.28	21	2.32	<1	3.96	4.1	0.150	36.6	0.43	9.2
0.44	29	2.90	3.0	4.62	23.3	0.225	49.1	0.50	12.2
0.78	44	3.48	5.8	5.28	69.5	0.301	57.9	0.64	19.4
2.24	93	4.06	9.5	5.94	94.0	0.451	81.4	0.93	27.0
2.45	92	4.64	16.5	6.10	102.0	0.526	85.9	1.21	38.8
2.77	98	5.21	24.0			0.601	87.9	2.14	62.8
3.13	103	5.80	33.5			0.676	88.6	2.86	76.8
3.88	104	6.09	42.0			0.751	96.0	3.36	90.4
		7.39	59.5						
		7.97	78.0						
		8.99	87.0						

TABLE A-5

ALACHLOR DESORPTIONS: EFFLUENT CONCENTRATION PROFILES

F-300 (7.03 gms)		XAD-4 (6.90 gms)		ES-865 (6.01 gms)		XE-340 (6.65 gms)		XE-348 (6.89 gms)	
gm CO_2 / gm adsorbent	Conc. wt fraction	gm CO_2 / gm adsorbent	fraction	gm CO_2 / gm adsorbent	fraction	gm CO_2 / gm adsorbent	fraction	gm CO_2 / gm adsorbent	Conc. wt Fraction
5.62	2.0×10^{-3}	2.86	23.27×10^{-3}	3.29	25.30×10^{-3}	14.86	1.52×10^{-3}	14.34	2.33×10^{-3}
11.25	2.3	5.73	60.70	6.57	42.93	29.73	0	28.69	0.51
16.87	2.5	8.59	34.40	9.87	43.50			57.38	0.25
22.50	2.5	11.46	26.81	13.17	14.67			86.07	0.10
28.12	0.51	14.32	20.23	16.45	13.66			143.45	0.18
33.74	0.51	20.05	12.65	23.02	2.78			200.84	0.03
39.36	0	28.65	5.56	32.89	0.34				
45.00	0	43.97	1.21	49.34	0.20				
50.58	0	57.30	0.91						
56.23	0	71.62	0.10						

TABLE A-6

ALACHLOR DESORPTIONS: PERCENT DESORBED

F-300 (7.03 gms)		XAD-4 (6.90 gms)		ES-865 (6.01 gms)		XE-340 (6.65 gms)		XE-348 (6.89 gms)	
gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed	gm CO_2 / gm adsorbent	% desorbed
5.62	5.2	2.86	10.6	3.29	16.9	14.86	79.5	14.34	17.8
11.25	11.0	5.73	35.5	6.57	45.3	29.73	79.5	28.69	21.7
16.87	17.5	8.59	53.74	9.87	74.3			57.38	25.6
22.50	24.0	11.46	65.9	13.17	84.1			86.07	27.1
28.12	25.3	14.32	75.1	16.45	93.2			143.45	32.6
33.74	26.6	20.05	86.6	23.02	97.0			200.84	33.3
39.36	26.6	28.65	94.2	32.89	97.6				
45.00	26.6	43.97	96.9	49.34	98.3				
50.58	26.6	57.30	98.9						
56.23	26.6	71.62	99.2						

GLOSSARY

Adsorbent Working Capacity: Effective adsorption capacity of an adsorbent for an adsorbate, weight per weight. This design parameter is usually lower than the virgin adsorbent adsorption capacity.

Adsorption Breakthrough Curves: Graph of adsorbate effluent concentration versus time, demonstrating the rise in concentration due to saturation of the adsorbent with adsorbate.

Regeneration: Process for restoring part or all of the adsorption capacity of a spent adsorbent.

Resin Adsorbents: Adsorbents manufactured from synthetic polymeric resins.

Supercritical Fluid Solvent: A solvent fluid at a pressure and temperature condition above the critical pressure and critical temperature.